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by

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# THE HEATS OF ADSORPTION OF SEVERAL GASES AND VAPORS ON CHARCOAL

BY FREDERICK G. KEYES AND MELVILLE J. MARSHALL

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## Introduction

Extensive measurements of the heat evolved when gases or vapors are adsorbed on charcoal and other substances have already been made. As early as 1874 Favre,[1] for example, determined the heat evolved for a large number of gases adsorbed on charcoal prepared from a variety of woods. The heat evolved per gram of gas adsorbed was found to be independent of the kind of charcoal, although the total amount adsorbed or the capacity was variable. The results of Favre were confirmed and extended later by Chappuis,[2] Titoff,[3] and Homfray[4] and recently by Lamb and Coolidge.[5] Homfray, however, instead of using a direct method, made an exhaustive study of the pressure-temperature concentration relation for argon, nitrogen, carbon monoxide, methane, carbon dioxide and ethylene. The Bertrand vapor-pressure formula ($p = G(T - a)^n/T$) was used to represent the constant-concentration relation between the pressure ($p$) and the temperature ($T$), $G$, $a$ and $n$ being constants in the equation. The heats of adsorption may, of course, be computed from the experimental data and constants given by Homfray. The values indicate that the heat of adsorption diminishes with increasing amounts of gas adsorbed.

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[1] Favre, *Ann. chim. phys.*, **5**, 1 (1874).

[2] Chappuis, *Wied. Ann.*, **19**, 21 (1883).

[3] Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

[4] Homfray, *ibid.*, **74**, 129 (1910).

[5] Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

The later careful experimental work of Lamb and Coolidge on the adsorption heats for organic vapors, wherein the charcoal was pumped out at 350° and to a pressure of 0.01 mm., showed that the adsorption heat was reproducible and decreased in a definite manner with the amount adsorbed. It was further clearly demonstrated that the heats of adsorption were practically independent of the capacity of the charcoal to adsorb large amounts of fluid. Interesting relationships were also pointed out connecting the heats of adsorption with the latent heats of vaporization, and the heat of compression under high pressure.

About the same time it was shown by Harned[6] that the presence of residual gases on the surface of the charcoal, even after prolonged heating in a good vacuum, influenced in a remarkable manner the *rate* at which gases or vapors were adsorbed. Thus chloropicrin adsorbed on charcoal (which had been heated to 900° and pumped for several hours) gave a rate of adsorption which was slow initially. It was only after repeated alternate heating and saturation of the charcoal with chloropicrin that the rate characteristics became reproducible. This fact indicates that the adsorptive process may be considerably interfered with by the presence of previously adsorbed material on the surface of the charcoal. It appears, therefore, that it might be preferable to "clean up" the charcoal with the particular gas before initiating observations in connection with the measurement of adsorption heats. It is quite likely, however, that this "residual-gas" effect demonstrated by Harned may affect the heat of adsorption only for the heats attending the first minute quantities adsorbed and is "swamped out" as soon as any considerable quantity is adsorbed. This in fact seems proved from the measurements of Lamb and Coolidge, since in their measurements the first heat of adsorption was measured for an amount equal to roughly 20% of the whole quantity of gas admitted to the charcoal. Thus in most cases the heat of adsorption for the smallest quantity whose heat of adsorption was measured, corresponded to a surface of charcoal covered by one or several layers of the adsorbing molecules. That there would be, in view of Harned's results, a measurable influence on the heat of adsorption until a *first layer* on the surface was completed, starting initially with a surface partially covered with foreign molecules, is at present neither definitely proved nor dis-

[6] **Harned, This Journal, 42, 372 (1920).**

proved, and the presence or absence of such an effect may be important in connection with the relation between surface catalysis and adsorption effects.

In a recent theory of adsorption due to Langmuir,[7] use is made of the hypothesis that the adsorbed molecule is held by either the "primary valence forces" or the "residual valence forces" of the atoms composing the adsorbing surface. At the surface of a piece of charcoal, for example, one of the primary bonds of each carbon atom would be unsaturated or at any rate partially free to exert an influence and one adsorbable atom or molecule would be bound for each surface carbon atom. Adsorption, therefore, Langmuir suggests, involves one layer only. On the other hand there is indication that very many layers of molecules must be attached in certain instances where substances are taken up by solids. Langmuir assumes in the latter cases that the material is condensed in the capillary spaces and only those molecules constituting the first layer are to be referred to as adsorbed. This layer, moreover, is to be considered as chemically or quasi-chemically united to the surface atoms of the adsorbent.

It may be supposed, however, that if, for example, oxygen molecules (or atoms) are attached to the surface carbon atoms by virtue of even secondary valence forces, the molecules, as such, will be in a special state of "valence strain" such as to enable this first layer to constitute of itself an adsorbing surface for a second layer of molecules of the same or of a different species. The state of "valence strain" in the second layer might, of course, be less in degree than for the first layer, but still conceivably sufficient to adsorb a third layer and succeeding layers similarly, until finally a layer was held attached in which the state of the molecules differed but little from the free state.

Even if it is conceived that the magnitude of the adsorption forces is sufficiently great to disrupt the oxygen molecules and cause the atoms to be held by the surface carbon atoms, it still appears likely that the second layer adsorbed would adsorb as a modified molecule and succeeding layers attach in a state of "valence strain" of continuously lessened degree. The point of view here suggested amounts then to accepting the thought that possibly primary[8] valence forces or secondary valence forces are involved in the phenomenon of adsorption but that the first adsorbed layer constitutes in itself a layer of molecules or atoms in a very special state (due to immediate proximity of the adsorbent), upon which additional molecules may adsorb to form a second layer, this layer and succeeding layers similarly partaking of the "special state" in a continuously lessened degree.

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[7] Langmuir, THIS JOURNAL, **40**, 1361 (1918).

[8] A certain hesitation is felt in using the terms "primary valence," "secondary valence," and "residual valence forces," for it is evident that the terms refer to qualities of atoms and molecules which cannot at present be precisely described or measured. The terms are used in this paper in the sense only of referring to qualities, a knowledge of which would permit an understanding of the manner of action of atoms one with another and, moreover, by what means molecular structure is maintained.

It is clear in any event that adsorption phenomena may be due to tremendous forces at the adsorbent surface which involve what is known as primary valence, or more feeble "residual valence" which manifests itself in a manner scarcely to be distinguished in its action from a uniform and homogeneous attractive force. As examples of the former, reference is made to the striking experiments of Langmuir, wherein oxygen atoms are held at extremely low pressures on the surface of tungsten and carbon filaments at very high temperatures. The other extreme is exemplified in the adsorption of substances such as water vapor or argon on charcoal.

Allusion has already been made above to the case wherein for an adsorbed substance the primary valence of, for example, a surface carbon atom was wholly or partially engaged, and the state of the resultant surface such as to enable the single layer of adsorbed molecules to exert an attraction for other molecules either of the same or different kind. It may well be that the state of strain of the molecular structure of the molecules in the adsorbed state is related to the phenomenon of surface catalytic action, since conditions favoring chemical reaction are thereby induced as a consequence of disturbing the normal conditions of equilibrium of atomic forces involved in preserving the existence of the molecule in the unadsorbed state.

The supposition has also often been made that in the adsorbed condition the molecules are attached to the surface by the same kind of forces as are called cohesional in the equation of state. If this were the universal fact the energies of adsorption of different species of molecules on the same adsorbing material should be some regular function of the cohesive constants in the equation of state of the respective species. Sufficient data are now available to enable a comparison of the cohesive constants with the adsorptive energies of different molecular species. It does not appear, however, that the simple cohesive pressure explanation of adsorptive action can account generally for adsorptive behavior. The adsorption of oxygen, for example, presents peculiarities which find no counterpart in the known adsorptive behavior of argon or water vapor.

In the experimental work described in the present paper the attempt has been made to measure the heats of adsorption for a variety of gases on the same sample of charcoal. Particular attention was paid to the case of oxygen due to the high chemical activity which oxygen manifests in the presence of carbon. Chlorine is of special interest also in this connection since Lamb and Coolidge, in their heats of adsorption work, found that compounds containing chlorine produced a "poisoning" effect on the charcoal such as to yield lower heats of adsorption when other substances were adsorbed on the chlorine-treated charcoal. The energies of adsorption for small concentrations[9] are therefore of particular interest.

### Experimental Method and Apparatus

The ice calorimeter was employed in all the measurements and the charcoal used was contained in a quartz tube which could be heated to 1000° and exhausted by means of a diffusion pump. Fig. 1 represents the disposition of apparatus used in the measurement of all substances except ether, chloropicrin and water, which were vaporized into the calorimeter from the liquid state. To measure the amounts the liquids were contained in calibrated capillary tubes.

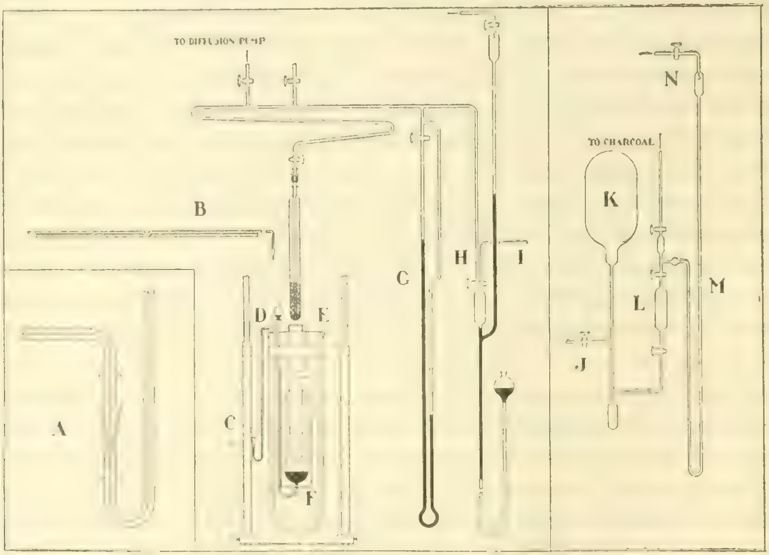

Fig. 1.

The first measurements were made by weighing the mercury displaced due to the melting ice within the calorimeter.[10] Later, a calibrated capillary tube B was employed which made connection with the calorimeter by means of a joint ground in such a manner as to cause practically no interruption of the capillary bore. The calorimeter was submerged in finely crushed ice, contained, in a 7.5-cm. Dewar tube set into a sliding

[9] The term concentration will be used hereinafter to denote the number of moles of substance adsorbed per gram of adsorbent.

[10] The ice may be very conveniently deposited in a uniform layer by placing a tube containing liquid ammonia inside the calorimeter. The mercury rises to the height of the ice mantle desired and serves to distribute the flow of heat very evenly. A tight rubber stopper and connecting rubber tube must be employed to lead away escaping ammonia gas, otherwise it will dissolve in the ice water within the Dewar tube.

support which permitted the calorimeter to be raised to receive the quartz tube containing the charcoal. To secure good heat conductivity between the charcoal and the calorimeter tube, mercury was placed in the ice-mantle tube sufficient to fill the space between the calorimeter tube and the former to a height above the level of the charcoal. The technique of using the ice calorimeter has been so fully developed and described elsewhere that further details will be omitted

In the cases of chloropicrin, water and ether, the liquids were freed from permanent dissolved gases by repeated distillation and the amounts adsorbed determined by noting the volume of liquid which disappeared from the capillary tube containing the liquid, immersed in a constant-temperature bath.

The method of measuring and introducing the gases varied somewhat with the conditions encountered. The ammonia and carbon dioxide were measured by means of an ordinary water-jacketed gas buret sealed *in situ*. The constant volume gas pipet H served for the oxygen, and the manometer G was used to measure the residual gas pressures over the charcoal. For chlorine, contained in K, sulfuric acid manometers had to be employed. The purified chlorine was frozen with liquid air and Bulb K pumped. The freezing and pumping process was repeated several times to insure the separation of dissolved air.

The charcoal used was a sample of that employed by the French government for gas masks during the war. It was graded to pass a screen having meshes 0.162 cm. and retained on a screen of mesh 0.132 cm. To remove the ash as completely as possible the charcoal was extracted in a Soxhlet extractor with hydrochloric acid for 24 hours and then with water for 48 hours. The charcoal was then warmed with hydrofluoric acid on a steam-bath and, after drying at 100°, extracted with water for 400 hours, during which time the water was changed every seven hours. The charcoal was finally dried at 150°. The reduction in ash content was as follows: ash content, original charcoal, 6.9%; after treatment with hydrochloric acid, 0.62%; after treatment with hydrofluoric acid, 0.36%.

The charcoal, before being used for the measurements, was baked at about 900° in the quartz tube until the pressure fell to about 0.0004 mm. This required in general from 12 to 20 hours. During the course of measurements with a given gas or vapor the charcoal was never allowed to come in contact with the air or any gas other than that under measurement. The weight of charcoal used amounted to 2.365 g. in the chloropicrin-water-ether series and 2.248 g. was employed for the remaining gases

The pure substances whose heats of adsorption were measured were as follows: oxygen, chlorine, carbon dioxide, ammonia, ether, chloropicrin and water. In each instance, a measured amount of substance was admitted to the fixed quantity of charcoal, and the amount of heat evolved computed from the displacement of the mercury corresponding to the volume displacement due to the melting of the ice mantle of the calorimeter.

After equilibrium had been obtained, a further quantity of vapor was admitted to the charcoal. A continuation of this portion-wise process of adding fluid was followed until the desired total quantity had been added. The amounts adsorbed will be given in moles per gram of charcoal. Moles will be in every case designated by $c$ while the integral heat of adsorption per g. charcoal actually measured will be denoted by $q$. The variation of the heat of adsorption per mole of substance at any particular ratio of substance to charcoal will be denoted by $(\partial q)/(\partial c)$.

The quantity $(\partial q)/(\partial c)$ was obtained graphically from large-scale plots using $q$ and $c$ as coördinates.

## The Experimental Results

Tables I–VII summarize the measurements carried out on the substances oxygen, chlorine, carbon dioxide, ammonia, ether, chloropicrin and water.

TABLE I

OXYGEN

| Series 1 | | Series 2 | | Series 3 | | Series 4 | | Series 5 | |
|---|---|---|---|---|---|---|---|---|---|
| $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ |
| 1.08 | 2.92 | 0.18 | 1.25 | 0.055 | 0.38 | 0.052 | 0.24 | 0.043 | 0.32 |
| 2.46 | 3.51 | .36 | 2.12 | .12 | .84 | .15 | .80 | .11 | .77 |
| 4.53 | 4.53 | 1.00 | 3.00 | .20 | 1.36 | .38 | 1.71 | .32 | 1.99 |
| .. | .. | 1.41 | 3.21 | .57 | 2.62 | .. | .. | .63 | 2.83 |
| .. | .. | 2.31 | 3.70 | 1.15 | 3.10 | .. | .. | 1.39 | 3.29 |
| .. | .. | 3.78 | 4.37 | .. | .. | .. | .. | 2.33 | 3.74 |
| .. | .. | 4.55 | 4.77 | . | .. | .. | .. | .. | .. |

| $c \times 10^4$ | $(\partial q/\partial c)_{\text{obs.}}$ | $(\partial q/\partial c)_{\text{calcd.}}$ | $c \times 10^4$ | $(\partial q/\partial c)_{\text{obs.}}$ | $(\partial q/\partial c)_{\text{calcd.}}$ | $c \times 10^4$ | $(\partial q/\partial c)_{\text{obs.}}$ | $(\partial q/\partial c)_{\text{calcd.}}$ |
|---|---|---|---|---|---|---|---|---|
| 0 | 72000 | 72000 | 0.3 | 43470 | 43000 | 1.0 | 5830 | 8370 |
| 0.1 | 67850 | 72000 | .4 | 27910 | 26500 | 2.0 | 5120 | 5710 |
| .2 | 61850 | 66000 | .5 | 20070 | 18420 | 4.0 | 4360 | 4575 |
| | | | | | | ∞ | 4000 | 4000 |

TABLE II

CHLORINE: 315 CC. PER G., N. T. P.

| Series 1 | | Series 2 | | Series 3 | | Series 4 | |
|---|---|---|---|---|---|---|---|
| $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ |
| 0.06 | 0.107 | 0.09 | 0.19 | 0.071 | 0.25 | 0.072 | 0.22 |
| .123 | .21 | .168 | .38 | .15 | .48 | .14 | .43 |
| .185 | .31 | .29 | .70 | .32 | .98 | .33 | .90 |
| .247 | .42 | .60 | 1.55 | .48 | 1.35 | 2.47 | 6.64 |
| .42 | .79 | .. | .. | .64 | 1.76 | .. | .. |
| .77 | 1.60 | . | .. | 1.78 | 4.89 | .. | .. |
| 1.14 | 2.25 | | . | .. | .. | .. | .. |
| 1.54 | 2.98 | | .. | .. | .. | .. | .. |
| 1.92 | 3.78 | | .. | .. | .. | .. | .. |

| $c \times 10^4$ | 0 | 0.1 | 0.5 | 1.0 | 2.0 |
|---|---|---|---|---|---|
| $\partial q/\partial c$ | 31900 | 31000 | 28100 | 25900 | 24600 |

### Table III

### Carbon Dioxide: 505.6 cc. per g., N. T. P.

| Series 1 | | Series 2 | | | |
|---|---|---|---|---|---|
| $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $\partial q/\partial c$ |
| 1.69 | 1.36 | 1.71 | 1.36 | 0 | 8410 |
| 3.55 | 2.72 | 3.64 | 2.61 | 1 | 7940 |
| 5.26 | 3.58 | 5.41 | 3.86 | 5 | 6588 |
| 8.41 | 4.81 | 7.37 | 5.09 | ∞ | 6000 |
| 13.94 | 6.85 | 9.34 | 6.47 | .. | .. |
| ... | .. | 11.13 | 7.67 | .. | .. |
| ... | .. | 13.96 | 9.67 | .. | .. |

### Table IV

### Ammonia: 1300 cc. per g., N. T. P.

| Series 1 | | Series 2 | | Series 3 | | | |
|---|---|---|---|---|---|---|---|
| $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $\partial q/\partial c$ |
| 1.55 | 2.28 | 1.81 | 2.06 | 1.67 | 2.24 | 0 | 16940 |
| 3.39 | 4.00 | 3.75 | 3.45 | 3.97 | 3.99 | 1 | 13160 |
| 5.17 | 5.43 | 5.79 | 4.83 | 6.74 | 6.24 | 5 | 7500 |
| 7.78 | 7.65 | 7.53 | 5.91 | 11.18 | 9.78 | 15 | 7160 |
| 11.38 | 10.64 | 9.16 | 6.85 | 15.56 | 13.15 | ∞ | 7000 |
| 14.32 | 12.42 | 11.95 | 9.42 | ... | ... | .. | ... |
| ... | ... | 15.57 | 11.57 | ... | .. | .. | ... |

### Table V

### Ether: 289 cc. per g., N. T. P.

| Series 1 | | Series 2 | | | | |
|---|---|---|---|---|---|---|
| $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $\partial q/\partial c$ | $\partial q/\partial c$, L. and C. |
| 1.75 | 2.64 | 3.23 | 5.24 | 0 | 15830 | ... |
| 4.37 | 6.28 | 6.56 | 10.13 | 2.5 | 15340 | 15850 |
| 8.49 | 12.18 | 10.37 | 15.09 | 5.0 | 14370 | ... |
| 12.79 | 17.49 | 13.98 | 19.26 | 10.0 | 12470 | . |
| 16.85 | 21.46 | 17.30 | 22.56 | 15 | 9550 | 13800 |
| 21.75 | 24.96 | 22.12 | 25.72 | ∞ | 7800 | ... |

### Table VI

### Chloropicrin

| Series 1 | | Series 2 | | Series 3 | | | |
|---|---|---|---|---|---|---|---|
| $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $\partial q/\partial c$ |
| 3.22 | 5.21 | 3.07 | 4.98 | 3.17 | 4.54 | 0 | 16600 |
| 6.68 | 10.14 | 6.72 | 10.15 | 6.34 | 8.94 | 5 | 14280 |
| 10.03 | 14.39 | 10.12 | 14.31 | 9.51 | 12.26 | 10 | 12130 |
| 12.30 | 17.51 | ... | ... | 11.44 | 14.17 | .. | ... |

### Table VII

### Water

| Series 1 | | | | Series 2 | |
|---|---|---|---|---|---|
| $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ | $c \times 10^4$ | $q$ |
| 9.21 | 7.86 | 45.6 | 46.42 | 9.04 | 7.67 |
| 17.94 | 17.18 | 54.9 | 56.01 | 18.20 | 16.40 |
| 27.10 | 26.85 | 64.2 | 65.88 | 26.68 | 26.01 |
| 36.6 | 36.81 | .. | | 36.31 | 33.52 |
| $\partial q/\partial c = 10510$ | | | | $\partial q/\partial c = 9460$ | |

Attempts were made also to measure the heat of adsorption of hydrogen, but sufficient accuracy was not attained with the present apparatus. The values of $(\partial q)/(\partial c)$ were in each case obtained from large-scale plots of the $q$, $c$ values listed in the tables.

There is no known functional relation between $q$ and $c$ except the two constant empirical equation $q = mc^n$ which sufficed to represent the results of Lamb and Coolidge. This equation gives for $(\partial q)/(\partial c)$, $mn(1/c^{1-n})$

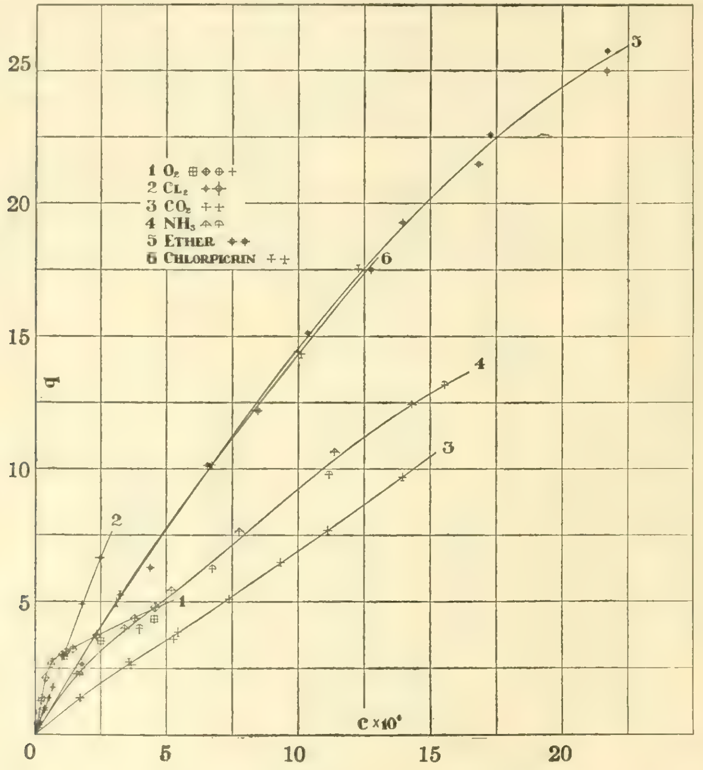

Fig. 2.

or $n(q/c)$. It has been found that for the present results this equation rectifies the data tolerably well except for oxygen. A rational equation is very much needed, however, and even an empirical equation of greater generality than the log $q$–log $c$ equation is much needed.

The data of the tables are plotted directly in Fig. 2 and again in Fig. 3, using as coördinates log $q$ and log $c$. The latter figure indicates that particularly for oxygen log $q$ is not proportional to log $c$ except at the smaller concentrations or again at the larger. In fact an inflexion exists. In the case of carbon dioxide on the other hand, the range of the data is not badly represented by a linear equation between the variables. There appears to be in this case, however, a trend slightly convex to the log $c$ axis. Ammonia exhibits a similar behavior, and also chlorine. Oxygen and ether, however, are concave to the axis of log $c$, although oxygen exhibits an inflexion at the higher concentrations. Chloropicrin is measured over too short a range to make comment of any value.

The case of oxygen is particularly striking when the quantity $(\partial q/\partial c)$ is considered. Fig. 4 indicates that as zero concentration is approached, about 72,000 cal. is evolved for one mole (32 g.) of oxygen adsorbed. The heat of formation of carbon dioxide from the monoxide and oxygen is

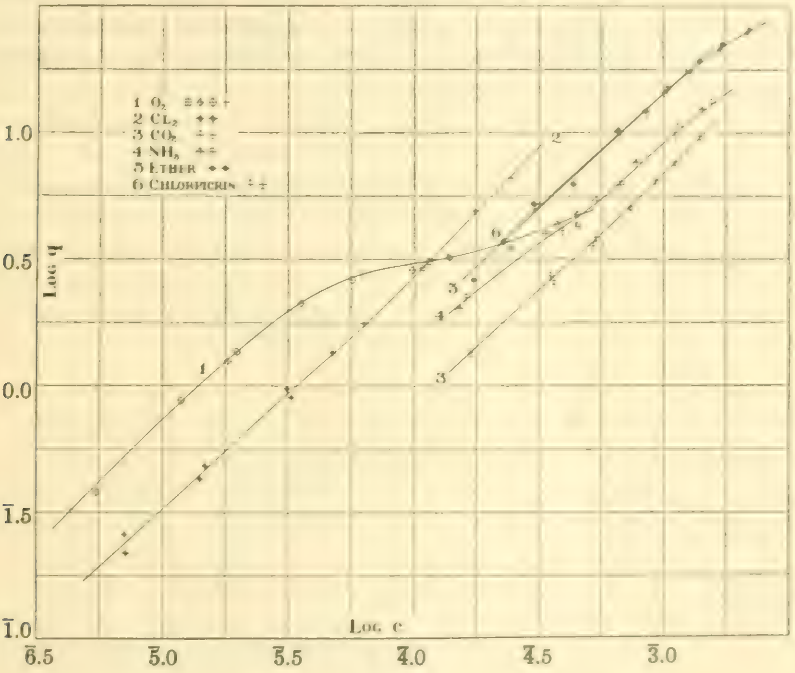

Fig. 3.

about this magnitude (69,000 cal.). There can be little doubt that the heating of the charcoal to 900°, however long, would not suffice to remove completely the unimolecular layer.[11] However, Blench and Garner[12] found from measurements carried out from 18° to 450° and at a concentration of $0.06 \times 10^{-4}$ moles of oxygen per g. charcoal that the molecular heat of adsorption at the higher temperature amounted to almost $3^1/_4$ times the heat at 0° while at 280° it is more than double.[13]

[11] Langmuir, **This Journal, 38,** 2221 (1916).

[12] Blench and Garner, *J. Chem. Soc.*, 125, 1288 (1924).

[13] Extrapolating the results of Blench and Garner at 18° to zero concentration, we find a number only slightly greater than 72,000 cal. for the heat of adsorption.

The huge temperature coefficient for the heat of adsorption as zero concentration is approached (340 cal. per degree) may be due to better experimental realization at the higher temperatures of a gas-free surface. The initial amounts of oxygen adsorbed would, in this case, first interact in such a way as to complete the first layer as oxygen atoms with the liberation of a large quantity of heat per mole of oxygen. An estimate of the heat of formation of carbon dioxide from gaseous carbon, for example, is approximately 400,000 cal. (heat of vaporization of carbon 287,000 cal., Fajans).[14] The difficulty with which Langmuir found carbon monoxide to be evolved from carbon filaments at 1300° to 2100° would seem to indicate that perhaps there would not be sufficient unattached adsorbent carbon atoms (46%) to account in this manner for the 224,000 cal. found by Blench and Garner at 450°.

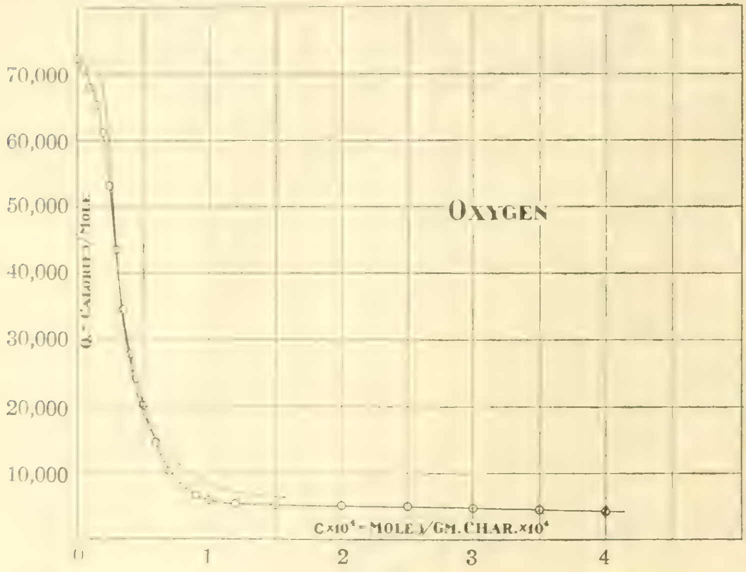

Fig. 4.

The general form of the curve (Fig. 4, for example) relating *q* to *c* indicates that many adsorbed layers are involved in passing from zero concentration at the ice-point temperature to the highest concentrations here measured ($4.5 \times 10^{-4}$ moles). It might be anticipated on the basis of the view of successive adsorbed layers herein assumed that a constant heat of adsorption should be obtained for each successive layer until completed. It is evident that after the formation of the first layer or even before its completion, a second or successive layers would begin to form at certain portions of the surface and instead of a broken curve a continuous diminution of heat of adsorption would result. The tendency to complete one layer at a time would depend on the intensity with which each layer was held, greatest for the first layer and less as the successive layers were less firmly bound. The kinetic energy of the particles approaching a surface in process of formation would also be a factor in the distribution of adsorbing particles. A rapidly moving particle, for example, impinging on a molecule belonging to a layer in the process of formation would tend to remain contributing to the next layer, whereas a slow-moving particle might be deflected under the attractive force and occupy a position in the layer being completed.

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[14] Fajans, *Z. Physik,* **1,** 101 (1920).

The attempt to deduce an equation connecting the molecular heat of adsorption in the successive layers as a function of the concentration has not been sufficiently successful to be worth recording. Empirically it may be observed, however, that $(Q_i - Q)/Q$ is zero initially and a constant when the heat becomes independent of the concentration. Thus the equation may be written, where $Q_i$ is the value of $\partial q/\partial c$ as zero concentration is approached and $Q_f$ the final value of $\partial q/\partial c$: $Q_i - Q = (Q_i - Q_f)f(c)$. The $f(c)$ is some function of the concentration which reduces to zero for $c \doteq 0$ and unity for $c \doteq \infty$. One form for $f(c)$ is $a/[c(e^{a/c} - 1)]$. The equation for $q$ then becomes

$$q = Q_i \int_0^c \frac{dc}{1 + \dfrac{Q_i - Q_f}{Q_f}\,\dfrac{a}{c(e^{a/c} - 1)}}$$

This equation satisfies the terminal requirement of the $q$, $c$ curve, for when $c \doteq 0$, $q \doteq Q_i c$, the heat evolved as the first layer is filled up for an amount of charcoal sufficient to be covered with a unimolecular layer or 32 g. of oxygen. Also when $c \doteq \infty$,[15] $q \doteq Q_f c$, which is the heat similarly given out as the final layers are completed. The $f(c)$ is unfortunately of such a form that the integral cannot be expressed in terms of ordinary functions. With $a = 1.44 \times 10^{-4}$ the values given in Table I under the column $(\partial q)/(\partial c)$ cal. have been computed. The dotted line in Fig. 4 is a graphic representation of the same computations.

The accord between the observed and calculated curves is perhaps as good as the present data warrant. Attention is directed to the fact that the part of the curve corresponding to small values of $c$ is relatively flat. As a rough approximation, assuming that this portion corresponds to the first layer, a value may be given for the active surface of the charcoal. The curve begins to fall at $c = 1 \times 10^{-5}$. If this in fact corresponds to the amount of oxygen per g. of charcoal required for the first layer, the active surface would be 5100 sq. cm. (the diameter of an oxygen molecule being taken as $2.9 \times 10^{-8}$ cm.). This estimate is far under previous-estimates by Lamb, Wilson and Chaney,[16] $1 \times 10^7$ sq. cm.; Williams,[17] $0.131 \times 10^7$ sq. cm.; or Lowry and Hulett,[18] $(0.16 \text{ to } 0.44) \times 10^7$ sq. cm.

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[15] The designation $c \doteq \infty$ is herein used as an abbreviated means of denoting a concentration of adsorbed substance sufficiently large to give $Q$ values substantially independent of the concentration.

It is worth noting that if the carbon atoms themselves were extended in a unimolecular layer, there would be $0.5 \times 10^7$ sq. cm. per g., or double this number if both sides of a carbon atom were available as an adsorbing surface.

The energy of adsorption for chlorine is likewise large initially, but the drop with increasing amounts adsorbed is not nearly as large as for oxygen. No special comment need be made beyond noting that charcoal is a good catalyst for the synthesis of phosgene from carbon monoxide and chlorine. It is not unlikely that a study of the heat of adsorption of both carbon monoxide and phosgene would provide sufficient data, with the energy of adsorption of chlorine gas, to suggest the mechanism of the catalytic action in this simple synthesis. The necessary measurements were originally planned as a part of the present investigation but could not be completed.

The substances carbon dioxide, ammonia and ether would not be expected to unite chemically with the carbon atoms in the first adsorbed layer. The energy of adsorption for the first exhibits a comparatively slight fall with increasing concentration, while ammonia shows a relatively large drop. The values for ether agree in the main with the results obtained by Lamb and Coolidge except that the decrease in the heat is greater at the higher concentrations. Thus at $c = 2.5 \times 10^{-4}$, $Q$ is 15,340 as compared with 15,850 obtained by Lamb and Coolidge, whereas at $c = 15 \times 10^{-4}$ Lamb and Coolidge find a value over 4000 cal. greater. The values for carbon dioxide and ammonia agree as well as may be expected with previous measurements by Chappuis and Titoff but the data of the latter are very much lower at the smaller concentrations.

The heat of adsorption of water is distinctly different in its relation to the concentration from the known behavior of other substances. The measurements recorded in Table VII are not as concordant as would be desirable since the second series gives a considerably lower average value of $\partial q/\partial c$ as compared with the first. The mean of both values of $Q$ although lower, does not differ greatly from the heat of evaporation of liquid water (10,600). There is an apparent tendency, it should be also noted, for $Q$ to increase with rising concentration rather than decrease.

Reference has already been made to the old idea that the cohesional forces of the normal gas or liquid phase may be the cause of adsorption phenomena. It has already been shown that in the case of oxygen the adsorption energy is enormous for the first small amounts adsorbed. The ordinary heat of evaporation of liquid oxygen is, in fact 45 times smaller. Even in the case of carbon dioxide, ammonia or ethyl ether the initial heats of adsorption are more than double the usual heat of evaporation of the liquids at 0°. The case of water is by comparison an apparent anomaly, for the heats of adsorption and evaporation are about the same.

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[16] Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, **11**, 430 (1919).

[17] Williams, *Proc. Roy. Soc.*, **96A**, 287 (1919).

[18] Lowry and Hulett, THIS JOURNAL, **42**, 1393 (1920).

During recent years investigations have been under prosecution in this Laboratory which have aimed to determine among other things the cohesive constants of certain selected substances. Of course for many years the constants $a$ and $b$ of van der Waals' equation have been available derived from "critical data," but since the equation is quantitatively inaccurate little use can be made of the constants. An equally grave difficulty has resided in the circumstance that the origin of the forces of cohesion has received no rational explanation until recently.[19] It appears clear as a consequence of Debye's work that the origin of these important forces lies (at least for certain types of molecule) in the induced polarization due to the displacement of the electric charges constituting the molecule by the electric field of the environing molecules. The force of attraction for the simpler molecules (no natural electrical moment) was shown to vary inversely as the ninth power of the distance and as the square of a function of the principal electrical moments of inertia of the molecule while the $A$ of the equation of state of one of the authors[20] is equal to $6\pi N^2\tau^2\alpha/5d^6$, where $\tau$ is the electrical moment of inertia function, $\alpha$ the polarization, $d$ the diameter of the molecule and $N$ the Avogadro number. At present too little is known of the actual structure of atoms or molecules to enable the quantitative development of these important ideas to proceed much further, but considerable insight may be obtained relative to adsorptive phenomena by a comparison of the $A$ and $\beta$ constants of the equation of state[21] with adsorptive energies.

Table VIII contains in Col. 4 the value of $4\ A/\beta$ which, per mole, may be considered to be the energy required to separate the molecules from their "actual volume" $\beta/4$ to infinity. The quantity $\beta$ since van der Waals' original work has been considered in its physical significance to be four times the volume of the molecules. There are many reasons for believing that the "volume" of a molecule is by no means the simple concept supposed before the development of the electrical theory of atomic and molecular structure. The quantity $\beta$ has, however, the dimensions of a volume, and for the present purpose may be considered as four times

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[19] Debye, *Physik. Z.*, **21**, 178 (1920).

[20] Keyes, *Proc. Am. Acad. Sci.*, **3**, 323 (1917).

[21] The equation of state referred to is $p = \dfrac{RT}{v - \beta e^{-\alpha/v}} - \dfrac{A}{(v + l)^2}$ where $A$, $\beta$, $\alpha$ and $l$ are constants and $A$ and $\beta$ are qualities analogous to $A$ and $\beta$ of van der Waals' equation. The constants given in Table VIII are taken in part from the published work of one of the authors and in part from investigations completed but unpublished.

TABLE VIII

| Substance | $A \times 10^{-6}$ $\frac{\text{cc.} \times \text{atm.}}{\text{mole}}$ | $\beta$ cc./mole | $4\,A/\beta$, cal. per mole | $(Q_f)_v$ obs./0° | $P_d$ |
|---|---|---|---|---|---|
| Ether | 31.3 | 460 | 6600 | 7250 | 54.1 |
| $H_2O$ | 19.0 | 230 | 8000 | 8914<br>9964 | 52.4 |
| $NH_3$ | 8.5 | 136 | 6060 | 6456 | 61.5 |
| $CO_2$ | 6.2 | 128 | 4680 | 5450 | 7.35 |
| $CH_4$ | 2.4 | 58.4 | 3980 | 4600 | 6.35 |
| A | 1.6 | 51.2 | 3032 | 3450 | 4.17 |
| $O_2$ | 1.5 | 44.5 | 3260 | 3454 | 4.10 |
| $N_2$ | 1.3 | 49.5 | 2540 | 3654 | 4.35 |
| $H_2$ | 0.16 | 19.3 | 804 | 1870 | 2.00 |
| He | .026 | 13.0 | 194 | 387 | 0.55 |

the apparent "volume effect" of the molecules. The fifth column contains what are believed to be the most reliable values for the energy[22] of adsorption at large concentrations. The first five values together with those for oxygen are taken from the measurements contained in this paper. The $Q_f$ values for argon, nitrogen, methane, hydrogen and helium have been selected from a consideration of the direct heat of adsorption measurements of Titoff and the $p$, $T$, $c$ data of Homfray. The number for helium (665 cal.) was taken from the very meager data of the latter and corresponds to a temperature interval 83° to 195°K. or a mean temperature of 139° instead of 273° to which all the other values refer. The work of Harned and the experimental findings in the present work, indicate that the outgassing or heating of the charcoal with frequent treatment of the adsorbent with the substance being investigated, should be a part of the procedure in securing data bearing on adsorption. Data for the monatomic gases are especially important since these, of all molecules, are most nearly without a natural electrical moment.

The sixth column contains a list of the constants of the dielectric-constant equation $V = 4N\pi\alpha/3 = P_d$, $(D - 1)/(D + 2)$ where $D$ is the dielectric constant, $V$ the volume of a mole and $\alpha$ the electrical polarization per molecule. It will be noted that the first three entries in the table are large numbers compared with those that follow. The former are molecules which possess natural electrical moments and do not accord with Maxwell's refractive-index relation $n^2 = D$. The last seven substances have no appreciable natural moments except carbon dioxide, whose moment is small (ten-fold less than that for ammonia).

In Fig. 5 a graphical representation of the data of Table VIII is presented in which $(Q_f)_v$, $4\,A/\beta$; $4\,A/\beta$, $P_d$; and $(Q_f)_v$, $P_d$ have been plotted. All three plots indicate simple relations between the variables. Of first importance is the close relation between the final energy of adsorption and the energy which the equation of state cohesive-pressure constant $A$ (dimensions, energy × specific volume) and the $\beta$ constant would indicate as the amount of energy required to separate the molecules from contact to infinity. It is clear that the final layers of molecules in the adsorbed state are not strained or in a state, from the point of view of inherent properties, which is very different (except for close packing) from that of the normal molecule. On the other hand this should not be taken as evidence that the so-called capillary theory of adsorption is favored.

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[22] The term "adsorption energy" is a convenient term for the heat of adsorption less the external work and will be used to denote this quantity throughout the paper.

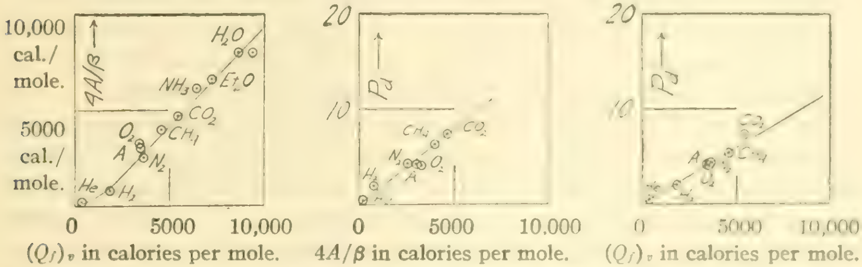

Fig. 5.—Plots showing relations among final heats of adsorption, dielectric properties and $p$-$v$.$T$ properties.

The high initial heats and their trend with increasing concentrations make it appear more useful to regard the adsorbed material as arranged in layers, the first of which partakes of a very special molecular state due to the combined electrical stresses set up by the close proximity of the adsorbent and adsorbed molecules. The second and succeeding layers are not under the direct influence of the adsorbent *per se* but of the already adsorbed molecules whose special state partakes in continually lessened degree of the state of the first layer.

The $(Q_f)_v$, $P_d$ plot is of considerable importance both from the point of view of adsorption theory as well as the molecular theory. The values of $P_d$ for the first three substances of Table VIII do not appear, since they are out of the scale of the plot. The remaining substances show proportionally between $(Q_f)_v$ and the induced polarization due to the field of the environing molecules. This may be taken as proof that for these substances the electrical moment of inertia function ($\tau^2$) divided by the diameter of the molecules to the eighth power is a constant (helium excepted). This may be easily seen by writing

$(Q_f)_v = K\,P_d = K\,(4/3)\,\pi\,N\,\alpha$, where $K$ is a constant;

$(Q_f)_v = F\,4\,A/\beta$, where $F$ is a constant.

and $K\,(4/3)\,\pi\,N\,\alpha = F\,4\,A/\beta$

or $K/F$ = constant $= 4\,A/\beta \times 1/(4/3)\,\pi\,N\,\alpha$,

since $A = (6/5)\,\pi\,N^2\,\tau^2\alpha/d^5$ and $\beta = (2/3)\,\pi\,N\,d^3$

$K/F$ = constant $= 27\,\tau^2/5\pi\,d^8$.

The quantity $216\tau^2\alpha/5\pi d^9$ would be the force with which two molecules of the non-permanent-moment type attract when the centers are at a distance equal to the diameter of a molecule. The high initial energy of adsorption would indicate that either $\tau^2$ was increased or that $d$ was diminished as a consequence of the adsorptive state. Tau is a function of the principal electrical moments of inertia (dimensions, charge $\times\ l^2$) and it is probable that both $\tau$ and $d$ are altered in magnitude. From the viscosity data of oxygen the diameter of the molecule at infinite temperature is $2.9 \times 10^{-8}$, while from the $\beta$ value it is $3.28 \times 10^{-8}$; thus, if $\tau^2$ remained constant the increase in $(Q_f)_v$ due to variation in diameter would be only 2.5-fold instead of 18-fold for oxygen, as appears to be the fact at zero concentration. Such a large change, as is the case here ($18\ Q_f = Q_i$), would seem to call for a very profound change in the molecule.

The theory of the cohesive pressure of molecules with large permanent moments is in too incomplete a state of development to permit any observations regarding the relation of the constants of these molecular species to the adsorption energies to be of much value. It would be very desirable, in this connection, to have measurements of the heats of adsorption at higher temperatures where the special effects due to the presence of permanent electrical moments in the molecule should vanish.

## Summary

1. Measurements of the heats of adsorption on charcoal as ash-free as possible have been made at the melting temperature of ice for oxygen, chlorine, carbon dioxide, ammonia, ether, chloropicrin and water.

2. In each case the heat of adsorption per mole is large initially (concentration $\mp$ 0) and falls rapidly to an apparently constant value with increasing concentration. In the case of oxygen the heat of adsorption is about eighteen times as great initially (72,000 cal.) as compared with the constant final heat (4,000 cal.).

3. The magnitudes of the final energies of adsorption have been shown to be proportional to the potential energy of the molecules from a state of "contact" to infinity based on a computation of the latter from the equation of state constants $A$ and $\beta$.

4. For molecules of the non-permanent electrical moment type, the energy of adsorption has been shown to be proportional to the electrical polarization of the molecule derived from dielectrical-constant data.

5. It is concluded as a result of the present investigation that adsorbed material can in general best be regarded as in a special state in which the first layer alone is to be considered as under the direct influence of the adsorbent. The first and succeeding layers, because of their special state, constitute new adsorptive surfaces which may adsorb molecules of the same species as the first layer or molecules of a different species. Each suc-

ceeding layer (the adsorbing molecules all of the same species) partakes of the special state of the first layer in lessened degree until finally a layer is reached wherein the molecular state differs little from what may be imagined as a molecular "contact" arrangement.

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# THE APPLICATION OF THE PHASE RULE TO GALVANIC CELLS

by

James A. Beattie

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# THE APPLICATION OF THE PHASE RULE TO GALVANIC CELLS

BY JAMES A. BEATTIE[1]

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The deduction of the phase rule by any of the many methods that have been used requires that the separate parts of the system under consideration be in equilibrium. It is therefore necessary, before proceeding to apply the phase rule to galvanic cells, to discuss them from this standpoint.

A system is in stable equilibrium when, if any of its internal variables (such as pressure, temperature, concentration, etc.) is slightly changed, the state of the system adjusts itself so as to oppose this change; and if this disturbing influence is removed, the system will restore itself to its original state. The case of neutral equilibrium, in which an infinitesimal disturbance of an internal variable causes no alteration in the state of the system, seldom if ever occurs in chemical systems and hence will not be considered here.

In general, galvanic cells, when their potentials are exactly balanced by an opposing electromotive force, as when measured on a potentiometer, may be considered to be in equilibrium.[2] Consider the concentration cell

$$\text{Pt, } H_2(1 \text{ atm.}) \mid \text{HCl } (C') \mid \text{HCl } (C'') \mid H_2(1 \text{ atm.}), \text{ Pt} \qquad A$$

when its potential is so balanced. If the applied electromotive force is slightly increased (other conditions being kept constant) current will flow through the system in such a manner as to transfer HCl from the more dilute to the more concentrated solution, thus increasing the potential of the cell; and if the external electromotive force is restored to its original value, current will flow through the cell in the opposite direction until the concentrations of the solutions are again $C'$ and $C''$. The other variables of the system can be treated in the same manner, and hence the system is in equilibrium.

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[1] National Research Fellow in Chemistry.

[2] Throughout this discussion the electromotive force of the cell is always considered as balanced by an equal and opposite potential. A cell that is in equilibrium under these conditions will also be in equilibrium when connected to a condenser (or, what amounts to the same thing, is on open circuit). Adding an electric charge to the plates of the condenser or subtracting one from them corresponds to increasing or decreasing the potential opposing that of the cell.

Certain cells, among which are those having electrolytes with only one ion in common, such as

$$\mathrm{Ag} \mid \mathrm{AgCl},\ \mathrm{NaCl}\ (C) \mid \mathrm{KCl}\ (C),\ \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{(B)}$$

have been found to give variable potentials when the liquid junction is made in the ordinary way, and hence are not in equilibrium. These cells will be discussed later.

It may be well to consider here the effect of diffusion. It is evident that Gibbs[3] believed that cells in which diffusion takes place are not equilibrium systems and hence not capable of phase-rule treatment. This is without doubt true, if the problem under consideration is the final state at which the system arrives after a very long time. There would then be no electrical potentials whatever present. It is now generally recognized, however, that in many cases several different equilibria are being established within the same system and that the phase rule is applicable to each, provided cognizance of this time factor is taken. Such is the case of the equilibria between liquid and vapor acetic acid and between acetic acid and its elements. It will be shown that in every galvanic cell containing a liquid phase, diffusion takes place. Yet, in general, with respect to the time necessary to establish and measure the electromotive force of the cell, the "state of the system" from a phase-rule standpoint has not changed due to diffusion (that is, the potential of the cell has remained constant) and hence a phase-rule discussion of these systems is in order. Several interesting cases, of which Cell B above is an example, where diffusion produces a practically instantaneous effect on the state of the system will be discussed later.

In all of the following discussion, the electrodes will always be considered reversible to the solution, that is, there are no irreversible effects such as overvoltage or passivity. The usual ideas regarding reversible processes are employed, namely, when current is allowed to flow through the cell the applied electromotive force must exceed that of the cell by only an infinitesimal amount.

In the application of thermodynamics to galvanic cells, it is convenient for purposes of writing the necessary equations to consider that the boundary between two phases at which a potential occurs is very thin, that is, the junction is so sharp that it is not necessary to treat the boundary portion as an extra phase. In experimentally measuring the potential of simple concentration cells similar to that shown at A it is often desirable to make a liquid-liquid boundary quite wide, but it has been shown that the potentials measured in this way are the same as those obtained when the liquid junction is made very thin by a flowing method.[4] However, if it is desired to consider the boundary portion as one or more extra phases, it will be shown later that the phase rule automatically takes care of this case.

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[3] "Scientific Papers of J. Willard Gibbs," Longmans, Green and Co., **1906**, vol. I, pp. 338, 429.

[4] MacInnes and Beattie, This Journal, **42,** 1117 (1920).

During the following theoretical discussion, the system will be treated as though diffusion does not take place at the boundary between two phases. The above assumptions define what Gibbs called a perfect electrochemical apparatus and, although no actual cell possesses all of these properties, we will have in mind the ideal case during the derivation of the phase rule, and study the effect of the deviations of actual cells from the ideal by an examination of several typical cases.

There are many methods of deducing the phase rule, but none, it appears to me, show so clearly the assumptions made and the relation between the variables as the derivation from the energy equation, which is the method used by Gibbs.[5]

## Galvanic Cells in which All of the Phases are under the Same Pressure

Let $\epsilon$ be the energy of any homogeneous part or phase of a system of $n$ components containing no electrical potentials. Then for any change, the differential of $\epsilon$ must satisfy the equation

$$\mathrm{d}\epsilon = T\mathrm{d}s - p\mathrm{d}v + \mu_1\,\mathrm{d}m_1 + \mu_2\,\mathrm{d}m_2 + \text{———————} + \mu_n\,\mathrm{d}m_n \qquad (1)$$

in which $T$ and $p$ are the temperature and pressure of the phase, d$s$ and d$v$ are the changes in total entropy and volume occurring, d$m_i$ the change in mass of the *i-th* component, and $\mu_i$ its chemical potential. If the system consists of $P$ phases, there is an equation similar to (1) for each phase.

If the passage of current through a system causes any of the components of a given phase to move through a boundary at which an electrical potential occurs there must be terms in the energy equation to take account of the fact that the total energy of the phase can be increased or decreased by the flow of electrical energy across this boundary. In galvanic cells a phase may contain one or two such boundaries; thus in Cell B each silver electrode contains one, and each liquid phase two. The electrical energy gained or lost by a phase at such a boundary is $E\mathrm{d}e$ and, since the potentials at the different junctions are in general different, there will be as many of these terms as there are surfaces containing potentials. Suppose that for a phase there are $q$ such surfaces; Equation 1 then becomes

$$\mathrm{d}\epsilon = T\mathrm{d}s - p\mathrm{d}v + \mu_1\,\mathrm{d}m_1 + \text{————} + \mu_n\,\mathrm{d}m_n + E_1\,\mathrm{d}e_1 + \text{————} + E_q\mathrm{d}e_q \qquad (2)$$

There is an equation similar to (2) for each phase containing an electrical potential at a surface through which any component moves upon the passage of current; and one similar to (1) for each phase at whose boundary such a process does not occur. It is evident that the same $E\mathrm{d}e$ term will occur in the equations for two adjacent phases. In the cell

$$\mathrm{Ag}\ \overset{E_1}{|}\ \mathrm{AgCl,\ HCl}\ (C')\ \overset{E_2}{|}\ \mathrm{HCl}\ (C''),\ \mathrm{AgCl}\ \overset{E_3}{|}\ \mathrm{Ag} \qquad (C)$$

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[5] Ref. 3, p. 96.

the term $E_1dc_1$ will occur in the energy equations for both the silver phase and the first liquid phase, and $E_2dc_2$, in the equations for the two liquid phases. The solid silver chloride phase which is used to keep the hydrochloric acid solutions saturated[6] contains no surface at which electrical energy takes part and hence the energy equation for this phase will contain no electrical term.

Before proceeding further it is necessary to consider the meaning of the terms *component* and *phase*.

The number of components in a galvanic cell can be determined by the usual rule,[7] namely, that it is the least number of independently variable chemical constituents, by means of which it is possible to express all variations in the composition of every phase of the system under consideration.

The number of phases present is determined by the number of energy equations similar to (1) or (2) that it is necessary to write. The addition of the electrical term sometimes causes phases to be counted as distinct which would otherwise be counted as one. In the cell (C) above, the two silver electrodes would be counted as two separate phases, since the potentials at the surfaces of each are different and hence their energy equations would be different. But the two solid silver chloride phases are counted as one since there is no electrical term in the energy equation, and hence the ordinary rule, that a solid phase is counted only once, applies. Moreover, an inert metal electrode such as the platinum in Cell A is considered as only one phase since, although there is an electromotive force at its surface, the metal does not migrate with the passage of the current, that is, the conduction is electronic and not electrolytic.

Cells containing a single solution between two electrodes should be considered as having two liquid phases (one saturated with the material at one electrode, and the other saturated with respect to the other) separated by a surface containing a potential. Tolman and Ferguson[8] have measured the potential of the cell, Pt, $H_2$ (1 atm.) | HCl (*C*), HgCl | Hg, which according to the above principle should be written, Pt, $H_2$ (1 atm.) | HCl (*C*, sat. with $H_2$) | HCl (*C*, sat. with HgCl) | Hg. They found that when they stirred the solution by bubbling the hydrogen through it the electromotive force of the cell was very variable. This would correspond to measuring the potential of the first cell. Later measurements by Ellis[9] and by Linhart[10] in which anode and cathode portions were kept separate gave higher and much more concordant results. This is to be expected since if some of the dissolved hydrogen came into contact with the calomel electrode, or calomel with the hydrogen electrode, the reaction would take place on the electrode rather than in the cell as a whole,[11] and this would reduce the electromotive force. If the mixing were thorough the potential of the cell would probably drop to zero.

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[6] In experimental procedure, the silver chloride is usually precipitated directly on the silver electrode, but theoretically the same result would be obtained by saturating the solution with AgCl, since its only function is to regulate the silver-ion concentration.

[7] It should be noted that the definition given by Washburn ["Principles of Physical Chemistry," McGraw-Hill Book Co., **1921,** p. 388] (that the number of components is one greater than the number of percentage compositions which it is necessary to state to fix the composition of the most complex phase) will not in general give the correct number of components for galvanic cells. This is evidently due to the fact that in such systems even the most complex phase may not contain all of the components of the system.

[8] Tolman and Ferguson, THIS JOURNAL, **34,** 232 (1912).

It will be shown that the application of the phase rule to cells of this type predicts that the first cell cannot be in equilibrium, and hence cannot give a constant potential, whereas the second is in equilibrium if its potential is properly balanced. In certain cells in which the essential reacting materials at the electrodes are so insoluble that practically no ions of these reacting materials, or at most only a few, exist in solution, mixing the anode and cathode portions of the electrolyte does not seem to affect the *measured* potential of the cell, but it is evident that for a thermodynamic discussion, these cells should be treated in the same manner as those containing more soluble substances at the electrodes.

Equation (2) contains as variables, the energy, temperature, entropy, pressure, volume, $n$ masses, $n$ chemical potentials, $q$ electrical potentials, and $q$ electrical charges, in all $2n + 2q + 5$. However, the partial differential equations, $\frac{\partial \epsilon}{\partial s} = T$ and $\frac{\partial \epsilon}{\partial v} = -p$, give two relations between $\epsilon$, $s$, $T$, $p$ and $v$. Also the $n$ equations, $\frac{\partial \epsilon}{\partial m_i} = \mu_i$, give $n$ relations between $\epsilon$, the $m$'s, and the $\mu$'s; and the $q$ equations $\frac{\partial \epsilon}{\partial c_i} = E_i$, give $q$ relations between $\epsilon$, the $c$'s and the $E$'s. These equations together with the original Equation 2 give $n + q + 3$ relations among the variables.

The $n$ masses can be split into $n - 1$ independent ratios of masses (or concentrations) and the total mass of the phase $M$. The *n-th* concentration is obtained by subtracting the sum of the $n - 1$ others from unity. Since the total mass of a phase does not affect equilibrium, this further reduces by one the number of independent variables. Hence the $2n + 2q + 5$ variables of Equation 2 are subject to $n + q + 4$ restrictions leaving $n + q + 1$ of them independent; in Equation 1 there are $n + 1$ independent. Any set of $n + 1$ independent variables can be chosen to fix the state of the phase under consideration.

Consider now a galvanic cell of $P$ phases, containing $S$ surfaces at which electric potentials exist. In writing the equations for the energy of the system we will assume that every phase contains some of each component, and later show how the equations are affected when such is not the case.

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[9] Ellis, THIS JOURNAL, **38,** 737 (1916).

[10] Linhart, *ibid.*, **41,** 1175 (1919).

[11] In order to get an electromotive force from a reaction it is necessary to separate it into two portions, one of which evolves electrons and the other absorbs them.

$$\begin{aligned}
\delta\epsilon' &= T'\,\delta s' - p'\,\delta v' + \mu_1'\delta m_1' + \text{———} + \mu_n'\delta m_n' + E_a\delta c_a \qquad (3)\\
\delta\epsilon'' &= T''\,\delta s'' - p''\delta v'' + \mu_1''\delta m_1'' + \text{———} + \mu_n''\delta m_n'' + E_a\delta c_a + E_b\delta c_b\\
&\vdots\\
\delta\epsilon^P &= T^P\delta s^P - p^P\delta v^P + \mu_1^P\delta m_1^P + \text{———} + \mu_n^P\delta m_n^P + E_S\delta c_S
\end{aligned}$$

The primes 1 to $P$ refer to the number of the phases; the subscripts 1 to $n$, to the number of the components, and the subscripts $a$ to $S$ to the number of surfaces containing electrical potentials. Some phases may contain only one such surface, some two, and some none, but for the derivation of the phase rule it is necessary to consider only the number of such surfaces, and not the way they are distributed among the phases.

Consider first the case in which there are no surfaces containing electrical potentials, nor any osmotic membranes in the system. When such a system is in equilibrium the variation of the total energy of the system must be zero or positive for all variations which do not conflict with the equations of condition of the system, which are that its entropy and volume are constant, and that the total quantity of each constituent remains unchanged. It has been shown[12] that in this case the necessary and sufficient conditions for equilibrium are that the temperature, pressure and chemical potential of each component be the same for every phase.

$$\begin{aligned}
T' &= T'' = \text{———} = T^P &&(4)\\
p' &= p'' = \text{———} = p^P &&(5)\\
\mu_1' &= \mu_1'' = \text{———} = \mu_1^P &&(6)\\
&\vdots\\
\mu_n' &= \mu_n'' = \text{———} = \mu_n^P
\end{aligned}$$

Each horizontal line represents $P-1$ equations, and there are $n+2$ such lines; hence there are $(P-1)\ (n+2)$ condition equations on the variables of the system, due to the various phases being in equilibrium.

In the case of a galvanic cell in which all the phases are under the same pressure, Equations 4 and 5 still hold, but not the set of Equations 6. This is due to the existence of electrical energy at the surface of some of the phases; also some phases do not contain all of the components of the system. It can be shown, however, that there are still the same number of equations between the chemical potentials as are given in 6.

In a galvanic cell, as shown at (C), there are three different types of equations between the chemical potentials.

(a) If there is no surface containing electrical energy between two phases, the chemical potentials of the components in the two phases are equal. This is the case of the dissolved and solid silver chloride.

(b) If a component is not present in a given phase, the $\mu\delta m$ term for that component will not appear in the energy equation for the phase under consideration. There will be as many $\mu$'s lacking in Equation 6 as there are components missing in the various phases. If the substance is a possible (though perhaps not actual) component, then the value of the chemical potential is equal to or greater than some value $M$ determined by the state of the system.[13]

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[12] Ref. 3, p. 65.

(c) If a component takes part in the passage of electricity from one phase to another there is still a relation between the chemical potentials in the two phases. Consider that the amount $\delta m_1$ of a component is transferred across a phase boundary by the passage, under equilibrium conditions, of a quantity $\delta c$ of electricity: then if all other factors are held constant the electrical and chemical works must be equal[14] or $\mu_1'\delta m_1 - \mu_1''\delta m_1 = E\delta c$; $\mu_1' - \mu_1'' = E\,\frac{\delta c}{\delta m_1}$. Now $\delta c/\delta m_1$ is the quantity of electricity necessary to transfer unit mass of the component, and is a constant for any given component; hence[15] $\mu_1' - \mu_1'' = KE$.

There is such an equation for every ion passing through a boundary containing an electrical potential. If two components take part in the passage of electricity through such a surface, as in the liquid junction between two electrolytes, there is a similar equation for each component, the same electromotive force being used in each case, but the appropriate value of $K$ substituted.

The above equation can be considered as a condition equation connecting the $\mu$'s for each ionic component, since the electrical potential $E$ has already been counted as a variable.

By means of the above considerations it can be seen that whenever one of the restrictions on the chemical potentials in (6) does not hold, another relation has been substituted, so that there are in the case of the galvanic cell as many relations between the chemical potentials as given in (6), that is $(P-1)n$. Hence, the total number of equations between the variables is $(P-1)\ (n+2)$.

Without counting the electrical potentials there are $n+1$ variables in each phase, or $P(n+1)$ in all and there are $S$ potentials making a total of $P(n+1)+S$. These are connected by the $(P-1)\ (n+2)$ equations; hence, the number of independent variables $V$ is equal to $n+2-P+S$.

Now if any arbitrary restrictions are placed on the system such as the fixing of the pressure, temperature, etc., the number of independent variations $V$ is further reduced by one for each of these arbitrary restrictions,[16] hence the complete algebraic statement of the phase rule becomes

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[13] Ref. 3, p. 66.

[14] Ref. 3, p. 333.

[15] If the pressures on the two phases are not the same, as in the case considered in a later paragraph, there is a term in this equation and the two preceding ones, taking account of the volume work done. There may be such a term even when the pressures on the two phases are the same, if the system is not subjected to the condition that its total volume must be constant. However, the equation still represents a relation between the chemical potentials, and does not involve any variables not already counted

$$V = n + 2 - P + S - R \tag{7}$$

When there are no electrical potentials in the system under consideration, Equation 7 reduces to the phase rule that is applied to ordinary systems.

*For every surface containing an electrical potential, the variance increases by unity; or for each surface containing an electrical potential the number of phases in which the system can be distributed is increased by unity.*

## Application of the Phase Rule to Specific Systems in which All the Phases Are under the Same Pressure

Before proceeding to apply the phase rule to galvanic cells it may be well to summarize what is meant by the various terms in the equation $V = n + 2 - P + S - R$.

The variance $V$ is the number of independent variables, that is, the number of variables it is necessary to specify to fix the state of the system.

The number of components $n$ can be determined by the rule given above.

The number of phases $P$ is the number of homogeneous parts of the system. Two electrodes of the same material at which there are different potentials are counted as two phases, in case the electrode material takes part in the passage of the current through the surface, and one phase when the electrode is inert. A single electrolyte containing two different electrodes must be divided into two phases separated by a surface containing an electrical potential, as in the first case given below.

The $S$ is the number of surfaces at which electrical potentials occur, and $R$, the arbitrary restrictions imposed on the system, such as the fixing of the temperature, pressure, etc.

**Case I.** Pt, $H_2(p \text{ atm.}) \mid HCl\ (C) \mid Cl_2(p \text{ atm.})$, Pt.—If the phase rule is applied to the cell *as written*, the computed variance is greater than the one experimentally found. There are four components, platinum, water, hydrogen and chlorine, four phases, and two surfaces containing electrical potentials.

Hence, $V = 4 + 2 - 4 + 2 = 4$. There are four variables—pressure, temperature, concentration of hydrochloric acid, and the electromotive force of the cell, of which only three are independent. Yet the phase rule states that there are four independent variables. This discrepancy shows that the system under consideration is not in equilibrium, which was the conclusion drawn from the work of Tolman and Ferguson in which they measured the potential of a similar cell, keeping the liquid phase homogeneous by stirring.

Suppose the cell is rewritten with an anode and a cathode phase, both containing hydrochloric acid of concentration $C$, but one saturated with hydrogen at $p$ atmospheres, and the other with chlorine, there being an electrical potential at the liquid junction, Pt, $H_2$ ($p$ atm.) | HCl ($C$, sat. with $H_2$) | HCl ($C$, sat. with $Cl_2$) | $Cl_2$ ($p$ atm.), Pt. There are still four components, but there are now five phases, three surfaces containing electrical potentials, and one restriction, namely, that the concentration of hydrochloric acid in the two liquid phases should be the same, whatever value $C$ may have. Therefore, $V = 4 + 2 - 5 + 3 - 1 = 3$; and, hence, if any three variables of the system are fixed, the state is entirely determined. The phase rule does not tell which of the variables are independent, but only the maximum number. Pressure, temperature, concentration of hydrochloric acid, the three junction electromotive forces $E_1$, $E_2$, $E_3$ and the total potential of the cell $E$ are all variables of the system, and fixing any three independent variables determines all the others. Thus if $E_1$, $E_2$ and $p$, or $T$, $p$ and $E_3$, or $T$, $p$ and $C$ are known, the state of the system is determined. In general, the latter case—the variation of the total potential of the cell with temperature, pressure and concentration of hydrochloric acid—is the one most often considered.

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[16] See Richards, This Journal, **38**, 983 (1916).

If the temperature and pressure are fixed, $R$ becomes 3 and $V = 1$. The potential is then a function of the concentration alone.

**Case II.** Ag | AgCl, LiCl ($C'$) | LiCl ($C''$), AgCl | Ag.—There are four components: silver, chlorine, lithium, and water. There are five phases: two liquid, solid AgCl, and two solid Ag, and three surfaces containing electrical potentials. Hence, $V = 4 + 2 - 5 + 3 = 4$, and the potential of the cell is determined by the pressure, temperature and two concentrations of lithium chloride.

If now a solution of lithium chloride of concentration intermediate between $C'$ and $C''$ is inserted between the two electrolytes—as is done in measuring the potential of the cell—the variance is not changed, since an extra phase and an extra surface containing a potential have been added, one of which affects $V$ negatively and one positively. Hence the phase rule indicates that the concentration of this intermediate solution (between limits, of course) is immaterial, which has been shown experimentally. We could also consider that an indefinite number of intermediate phases exists, each with an additional potential, *i. e.*, that the concentration of the intermediate solution varies gradually from $C'$ to $C''$.

**Case III.**—Consider the application of the phase rule to the cell, Ag | AgCl, KCl ($C$) | NaCl ($C$), AgCl | Ag, in which the molal concentration of the two solutions is the same. There are five components, five phases, three surfaces containing potentials, and the one restriction that the two concentrations of the electrolytes shall be the same.[17] Hence,

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[17] The phase rule does not indicate any particular mode of expressing concentration. Yet even on any basis (such as percentage by weight) there would be a restriction, namely, that the fraction of chloride-ion constituent in the two liquid phases shall have a certain ratio.

$V = 5 + 2 - 5 + 3 - 1 = 4$. The variables of the cell are the pressure, temperature, concentration $C$, and the electromotive force. It is natural to suppose that only three of these are independent, yet the phase rule gives a variance of four. This would indicate either that this cell is not in equilibrium, or that the various quantities appearing in the phase rule have not been correctly counted. In either case the phase rule predicts that there is something peculiar about this cell. Lamb and Larson[18] have studied cells of this type, in which the solutions have only one ion in common, and they found that the potentials were variable unless the liquid junction was made in a particular way, by means of a "flowing junction." That is, when the liquid junction is made by the ordinary static method (even if diffusion is reduced to a minimum by the use of a ground glass connection at the boundary), the system is not in equilibrium, since the potential of the cell varies with the time. The fact that the use of a flowing liquid junction[19] caused the potential to become constant shows that the irreversibility in the cell with a static junction is at the liquid junction itself.

This method of fixing the potential at a boundary by a particular process removes the cause of the system not being in equilibrium, and hence may be considered as a restriction placed on the cell so as to make it behave as if in equilibrium. In the phase-rule equation there are then two restrictions, whence $R = 2$, so $V$ becomes 3, and the system is trivariant as would be expected.

In general when the calculated variance is greater than is expected, it indicates that the system, as written, is not in equilibrium, for the reason (a) that the system was not correctly divided into phases; or (b) that the system under consideration *cannot* be in equilibrium; or (c) that some additional restriction, or restrictions, must be imposed so as to remove an irreversibility from the system.

The particular method of determining what restriction is necessary to cause the system to be in equilibrium is, of course, a matter for experiment for each case. All that the phase rule predicts is that the cell will not be in equilibrium when the connections between phases are made in the usual manner.

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[18] Lamb and Larson, THIS JOURNAL, **42,** 229 (1920).

[19] The difference between a static and a dynamic liquid junction is evidently that in the former case, any concentration change due to diffusion that occurs, persists and becomes greater as time goes on, but in the latter case such changes are immediately destroyed by the production of a fresh boundary. In some cells, such as the ordinary concentration cell, diffusion does not affect the liquid junction potential, but in the cell under consideration it evidently does. In an earlier paragraph a distinction was made between an irreversibility which changes the state of the system from a phase rule standpoint and one which does not. An example of the former is diffusion in the cell considered in Case III, and of the latter diffusion in the cell of Case II.

### Galvanic Cells in which the Phases Are under Different Pressures

To illustrate the application of the method given above for deducing the phase rule for any system, consider a cell in which all the phases are not under the same pressure. Suppose that in the system under consideration there are $\pi$ different pressures.

It will not be necessary to rewrite the energy equations, but only to consider the change introduced in Equations 4, 5 and 6. Not counting the pressures or electrical potentials, there are $n$ variables in each phase, and $nP$ variables in the $P$ phases. In addition, there are $S$ electrical potentials, and $\pi$ different pressures, or $Pn + S + \pi$ variables in the system. Equation 4 still holds, and there are also, as before, $(P-1)n$ equations conditioning the $Pn$ chemical potentials, which gives $(P-1)\ (n+1)$ equations connecting the variables of the system. The variance then becomes

$$V = Pn + S + \pi - (P-1)\ (n+1) = n + 2 - P + S - R + (\pi - 1) \qquad (8)$$

This is the general equation for any galvanic cell of $n$ components distributed in $P$ phases, separated by $S$ surfaces containing electrical potentials and under $\pi$ entirely different pressures. Equation 7 is a special case, in which all the phases are under the same pressure, that is, $\pi = 1$.

As an example take the cell Pt, $H_2$($p_1$ atm.) | HCl ($C$ molal $p_2$ atm., sat. with $H_2$ at $p_1$ atm.) | HCl ($C$ molal $p_2$ atm., sat. with $H_2$ at $p_3$ atm.) | $H_2$ ($p_3$ atm.), Pt. There are four components, five phases, three surfaces with potentials, three different pressures—$p_1$, $p_2$ and $p_3$—and the restriction that the hydrochloric acid concentration in the two liquid phases shall be the same. The variance is $V = 4 + 2 - 5 + 3 - 1 + (3 - 1) = 5$, and the system becomes nonvariant when the temperature, concentration of hydrochloric acid, and the three pressures are fixed.

### General Derivation of the Phase Rule

The method given above of deriving the phase rule is applicable to any system in equilibrium, if the energy equation can be written for each phase. The general energy equation has the form

$$d\epsilon = T ds - p dv + \mu_1 dm_1 + - + \mu_n dm_n + A_1 da_1 + A_2 da_2 + - \qquad (9)$$

where $A_1$, $A_2$— are intensity factors and $a_1$, $a_2$— capacity factors of the various forms of energy (other than heat, volume and chemical energy) manifested in the phase.

There must be a term in Equation 9 for each way that energy can leave or enter the phase. Hence, to determine what variables it is necessary to consider as affecting the equilibrium, it is only necessary to find out those that affect the energy of the individual phases.

Thus in disperse phases, the extent of division of the phase will not affect the equilibrium unless the particles are small enough to require a term for the surface energy, $\gamma_1 dS_1$, in the energy equation, $\gamma$ being the surface tension and $S$ the surface. If such a term is required, the equilibrium is affected by the state of division of the phase, and the phase rule derived for this system would be different from that ordinarily given. It is also evident that all the particles must be the same size so that $\gamma$ is the same for each one; if several sizes of particles are allowed there must be a term in the energy equation for each size since $\gamma$ would be different for each. It is easily seen that the phase rule derived for a system containing $S$ different surface tensions would be the same as that for a system having $S$ surfaces containing potentials, namely, $V = n + 2 - P + S - R$, $S$ now representing the number of numerically different surface tensions in the system.

This equation was deduced in a somewhat different manner by Pavlov[20] and also by Tolman,[21] but it seems that the derivation from the energy equation is the most direct, and gives the best information as to what variables it is necessary to consider as affecting the equilibrium.

## Summary

It has been shown how the phase rule can be deduced for any system in equilibrium.

The phase rule has been deduced for galvanic cells when in equilibrium, the variance being given by the expression, $V = n + 2-P + S-R + (\pi-1)$, where $n$ is the number of components distributed in $P$ phases, separated by $S$ surfaces containing electrical potentials, and under $\pi$ different pressures. $R$ is the number of arbitrary restrictions imposed. In general all the phases are under the same pressure, and in this case, $V = n + 2-P + S-R$.

When the variance calculated by this equation is greater than that expected, it indicates: (a) that the system was not correctly divided into phases or, (b) that the system under consideration cannot be in equilibrium or, (c) that some additional restriction, or restrictions, must be imposed so as to remove an irreversibility from the system.

The phase rule has been applied to several cells. The following points have been made.

(a) The number of phases is determined by the number of energy equations it is necessary to write. Thus two silver electrodes having different potentials at their surfaces must be considered separate phases, since their energy equations are different. The same applies to two colloidal phases of the same material but with different surface tensions.

(b) A cell containing two electrodes and one solution must be considered as having two liquid phases (one saturated with the material at one electrode, and the other saturated with respect to the other) separated by a

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[20] Pavlov, *Z. physik. Chem.*, **75**, 48 (1910).

[21] Tolman, THIS JOURNAL, **35**, 307, 317 (1913).

surface containing a potential; and the cell is not in equilibrium and hence will not give a constant electromotive force, if the two portions are mixed.

(c) Cells containing a liquid junction between two solutions having a single ion in common are not in equilibrium unless there is a restriction placed on the method of making the liquid junction, so as to remove an irreversibility at this boundary.

Cambridge A, Massachusetts

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# THE EQUATION OF STATE FOR METHANE GAS PHASE*

By FREDERICK G. KEYES, LEIGHTON B. SMITH
and DAVID B. JOUBERT

The isotherms for gaseous methane have been measured by Amagat.[1] The absolute volumes are not given, but merely the volumes relative to the capacity of a certain manometric tube. The data extend from 14.7° to 100.1° and over a pressure range of 40 to 300 atms. Aside from the relative pressure-volume products of Amagat there are no data from which the constants of the equation of state for the gas phase can be evaluated. Moreover, the question of purity is of importance, and Amagat at the time (1880) did not have the facilities for insuring the purity of a hydrocarbon such as methane. In the present investigation the attempt has been made to measure the isometrics of methane between 0° and 200° and over a pressure range from about 36 to 300 atms.

There are advantages experimental and theoretical in choosing the "isometric method" of investigating the pressure-volume-temperature relation for a fluid. Of the three quantities the volume is the most difficult to measure and control and in the attempt to keep the volume constant attention is particularly focused upon the conditions necessary accurately to maintain a chosen volume. The theoretical work in connection with the equation of state[2,3,4,5,6,] has made it seem highly probable that in the case of a fluid composed of molecules of invariable type, the pressure should vary linearly with the temperature at constant volume. The attempt to test this linearity of pressure increase directly makes it further desirable to employ the isometric method. In fact, the investigation of the sources of error in the methods used to carry out measurements at constant volume has led by successive approximations to considerable improvements in the apparatus. The relatively simple form of the equation of state for a fluid composed of invariable molecular species requiring the pressure to be linear in the pressure-temperature relation makes it, moreover, comparatively easy to determine the constants of the equation of state.

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* This work is published by permission of the Director of the Bureau of Mines. The present paper together with the other papers of this number are some of the investigations required by the Bureau of Mines in perfecting the processes for the extraction of helium from natural gas.

This investigation was undertaken by the Massachusetts Institute of Technology at the request of the Bureau of Mines, working in cooperation with the War and Navy Departments. The Bureau of Mines as well as the Massachusetts Institute of Technology contributed liberally in funds needed to carry forward the work. The funds of the Bureau of Mines were allotted from Army and Navy appropriations made available for research work connected with extracting helium from natural gas.

[1] Amagat, Annales de Chimie et de Physique **22**, 367, 1881.

[2] Phillips, Jour. of Math. and Phy. M. I. T. **1**, 42, 1921.

[3] Phillips, Proc. Nat. Acad. Sci. **7**, 172, 1921.

[4] Keyes, Jour. Amer. Chem. Soc. **43**, 1452, 1921.

[5] Keyes, Jour. of Math. and Phy. M. I. T. **1**, 89, 1922.

[6] Keyes, Proc. Nat. Acad. Sci. **3**, 323, 1917.

In the investigation here presented it was hoped to improve materially the accuracy with which a given volume could be maintained and reproduced. The pressure measurements also have been improved from the point of view of accuracy and sensitiveness. The temperature measurements made by means of the platinum resistance thermometer were found at the conclusion of the measurements not to be as reliable as was at first thought. This circumstance was due to defects in the resistance bridge which, however, after having been discovered, proved not to invalidate the temperatures by more than probably 0.1° at most. Of course temperatures are desired on the absolute temperature scale, and the comparisons of the platinum thermometer with the gas scale leave uncertainties at present which may amount to 0.1° at 200°.

The present data on methane are the most nearly linear of any pressure-temperature data thus far examined and verify the particular form of the equation of state. Considerable improvement in the apparatus doubtless can be realized in future work, however, and a still more accurate test made of this most important relation.

### Preparation of Pure Methane

The methane was prepared by heating a mixture of dry sodium acetate and soda-lime. The diagram, Fig. 1, illustrates the apparatus employed for generating and purifying the gas. The dry powdered sodium acetate and soda-lime were contained in

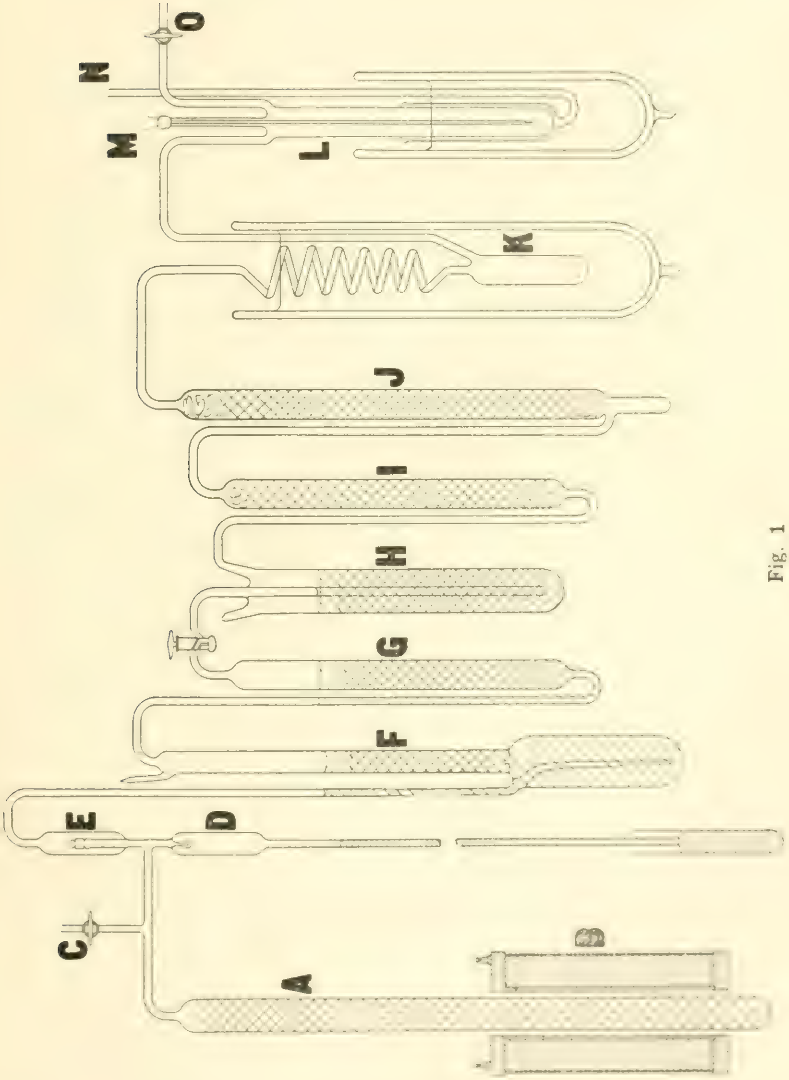

Fig. 1

the pyrex tube A about 2.5 cm. in diameter and 50 cm. in length. The salt mixture could be heated regularly and the gas evolution controlled by the movable electric furnace B. A safety valve was provided by the barometric mercury column D, while a Bunsen type valve, consisting of a band of rubber covering a small hole in the glass reëntrant portion at E, prevented surges in the liquid purifying tubes. Evacuation of the salt mixture tube was secured through C, while F contained 20 per cent fuming sulphuric acid employed to retain acetone or unsaturated hydrocarbons. Quite a proportion of acetone is formed in the acetate soda-lime reaction. The tube G contained 98 per cent concentrated sulphuric acid to absorb $SO_3$ fumes and H 20 per cent caustic soda solution followed by solid caustic I for the removal of $CO_2$. The tube J containing $P_2O_5$ served finally to dry the gas which was condensed by means of liquid air in the receiver K, whence it could be distilled back and forth from K to L to remove hydrogen and other gases. The tube L was double-walled and silvered, but arranged so that the double-walled portion could be exhausted or made conducting by admitting hydrogen. The thermocouple M sufficed to observe the constancy of melting of the solid methane within L. The frozen methane was pumped at O. The purified material was finally allowed to expand through O into a five-liter globe which previously had been exhausted hot to remove adsorbed moisture and other gases. A special analysis apparatus was a part of the system and will be presented in a later paper dealing with the isometrics of nitrogen-methane mixtures. The analytical apparatus indicated that foreign gases were not in excess of one part in 500, which was the limit of accuracy attainable from the apparatus at the time. From the precautions taken in the preparation the purity of the methane would have been greater than the analysis indicated.

## The Pressure Gauge

The gauge was similar in construction to the gauge employed by Keyes and Brownlee[7] except that the floating piston was of about 1 cm. diameter. Improvement has been made in the

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[7] Keyes and Brownlee, Jour. Am. Chem. Soc. **40**, 25, 1918.

## TABLE I

### Calibration of the Pressure-Measuring Piston

| *Mean Temp. of Column* | *Total Corr. Weight Grams* | *Height in mm.* | *Corr. for Oil Level* | *Corr. for Tape Length* | *Mm. at* 0° | *Constant of Piston mm./g.* | *Per Cent Dev. from Mean Value* 1.0255 |
|---|---|---|---|---|---|---|---|
| 19.30 | 8490.85 | 8826.0 | −85.1 | .... | 8708.3 | 1.02560 | +0.010 |
| 19.07 | 8464.75 | 8798.5 | −85.1 | +0.9 | 8682.4 | 1.02575 | +0.024 |
| 18.66 | 8287.67 | 8613.5 | −85.1 | +0.7 | 8498.4 | 1.02543 | −0.007 |
| 18.66 | 7487.30 | 7790.0 | −85.1 | +0.1 | 7677.2 | 1.02536 | −0.014 |
| 18.32 | 7036.82 | 7327.5 | −85.1 | +0.4 | 7217.2 | 1.02562 | +0.012 |
| 19.13 | 6685.74 | 6968.0 | −85.1 | +0.1 | 6857.7 | 1.02557 | +0.020 |
| 19.36 | 6208.53 | 6475.0 | −85.1 | +0.1 | 6366.2 | 1.02540 | −0.010 |
| 19.19 | 6043.33 | 6305.0 | −85.1 | +0.1 | 6197.0 | 1.02544 | −0.006 |
| 19.23 | 5572.50 | 5820.5 | −85.1 | +0.1 | 5714.2 | 1.02543 | −0.007 |
| 19.49 | 4759.30 | 4984.0 | −85.1 | −0.1 | 4880.6 | 1.02547 | −0.003 |
| 18.85 | 4413.13 | 4627.5 | −85.1 | −0.2 | 4525.8 | 1.02553 | +0.003 |
| 18.85 | 3464.68 | 3650.0 | −85.1 | ..... | 3552.0 | 1.02520 | −0.024 |

Mean Value of Constant 1.0255 mm. per gram.

mercury column used to calibrate the gauge. This consists in using a platinum needle for electrical contact at the surface of the mercury in the short arm of the column to facilitate detecting the equilibrium of the column. Better temperature control of the column was also secured by enclosing it in a channel-shaped support closed on the open face by adjustable pieces of cardboard. The equilibrium of the piston was determined by the use of a telephone using an audion bulb as shown in diagram Fig. 2. This device enabled a very feeble current to be used at the surface of the mercury, avoiding emulsification of the oil, which seems to take place when the secondary of an induction coil is used to indicate contact of the mercury with the needle. The emulsification is of very great importance in making compressibility measurements with the apparatus of Fig. 2, since emulsification of the mercury and oil amounts to removing a small quantity of mercury from the piezometer portion of the system.

The length of the mercury column was measured on a steel tape stretched by a load of seven kilos. The calibration of the tape was effected under the same stretching load by comparison with a standard meter compared at the United States Bureau of Standards. Table I gives a summary of the data from which it will be seen that the maximum deviation from the mean is about one part in four thousand, while the average deviation is about one part in eight thousand.

## The Compressibility Apparatus and Method of Loading the Piezometer

The general apparatus is shown in Fig. 2, which is a further development of the apparatus used by Keyes and Felsing[8]. The floating pressure piston with scale pan and motor for oscillating the piston is represented at J, L, and K. The oil injector I serves to adjust the height of the floating piston and to compensate for leak of oil around the floating piston. The steel block C contains a stopcock V for exhausting and a mercury-level-indicating insulated needle D. This contact serves to detect equilibrium of the load on the piston and the pressure exerted by the material in the piezometer. For example, if too great a weight is on the piston the mercury will be depressed and if too small a weight it will rise and make contact. One gram suffices, as a rule, to make or break the contact. A shut-off is provided for closing the piezometer B from the entire apparatus while connection is made from the block C to the mercury volume-displacement piston apparatus G submerged in a constant temperature bath F, whose contents are stirred by means of the motor and propeller apparatus Q. The nut H serves to force the piston into the mercury, driving it through fine steel tubing into the piezometer. The advance of the piston is indicated by one hundred divisions engraved on the under portion of the nut. Whole turns are counted by a " cyclometer " not shown in the drawing. It is possible with the 16 mm. piston driven by a 7.1 threads per cm. screw to estimate 0.001 turn of the nut corresponding to about 0.00028 c.c. The packing of the piston which moves into the cylinder G consists of cotton fabric heated in ceresin wax to 160°, and hard rubber forced into place by means of a steel ring driven by a screw cap.* The packing is perfectly tight over long

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[8] Jour. Am. Chem. Soc. **41**, 589 1919.

* The diagram, Fig. 2a, shows the method of applying the packing to the piston in the mercury volume injector. The piston is represented by A and the nut driving the packing at B through pressure on the steel ring D. At the bottom of the packing gland is a steel ring H which also is a snug fit to the piston. E, E indicates hard rubber rings and F, F, F the cotton fabric (such as unbleached cotton) impregnated quickly with ceresin wax at

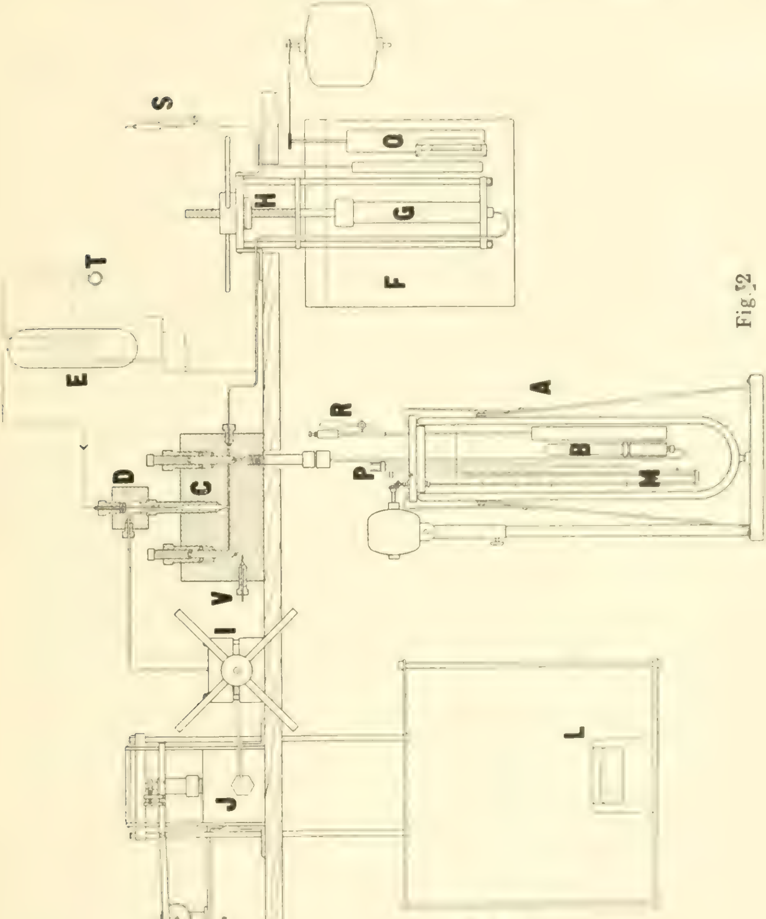

Fig. 2

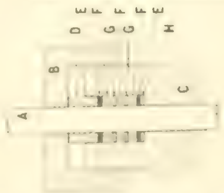

Fig. 2a

160°. G, G are rings of soft steel. The annular width of the packing gland is about 3 mm. and the depth for moderate pressures (500 atms.) about 3 to 4 cm. The hard rubber ring protects the waxed packing from the [illegible] of the bath and serves to wipe the piston as it moves backward and forward, thus minimizing the removal of wax. This latter objective is not as satisfactorily accomplished as desirable, but no better method of wiping the piston has been applied.

periods of use after having been seasoned by exposing it to several hundred atmospheres with successive tightenings of the driving nut. A similar packing is used on the stopcocks of the block C.

The constant temperature bath represented at A, Fig. 2, consists of a pyrex Dewar tube 6.6 cm. in inside diameter and 40 cm. in length. The disposition of the platinum thermometer, stirrer, heater and mercury in the steel regulator is evident from the figure. For the bath fluid a high boiling light oil sufficed for the range 50° to 200°, while an ice bath served to maintain the piezometer at 0°. The cover of the bath is of asbestos wood and carries the bearing for the stirrer and binding posts for the electrical connections of the heater. The Dewar tube bath here represented is very convenient and has been employed to 330°. It possesses obvious advantages due to its permitting a view of the interior at all times and the heat insulation is excellent. The Dewar tube, however, requires prolonged heating at 450° during exhaustion. Recent tubes silvered in such a manner as to leave a clear strip 2 cm. to 5 cm. in width parallel to the long axis have greater heat-insulating properties, at the same time permitting a view of the interior. The silver will not peel off once it has been slowly and thoroughly baked out during exhaustion.

The piezometer is represented in detail at A, Fig. 3. It was made in one piece from cold rolled steel, the lower end being spun shut and welded with the oxy-acetylene flame. A left-hand thread was cut on the outer portion, where it screwed into the top piece E surrounded by a cooling coil of copper B. The latter piece carried a screw driver F passing through a packing gland and sealed with mercury. The piezometer was locked by means of the plug D, which had a 0.75 mm. hole drilled throughout its length. The locking of the piezometer was secured by the compression of the gold washer C against a seat in the piezometer by means of the screw D. The purpose of the cooling coil about E was to preserve the packing gland during the exhaustion of the bomb at 350°.

Methane is, of course, above its critical temperature at ordinary temperatures, and it was necessary to place in the piezometer sufficient methane to give a range of volumes per gram from 8 c.c. to 35 c.c. over the temperature range 0° to 200°. The capacity

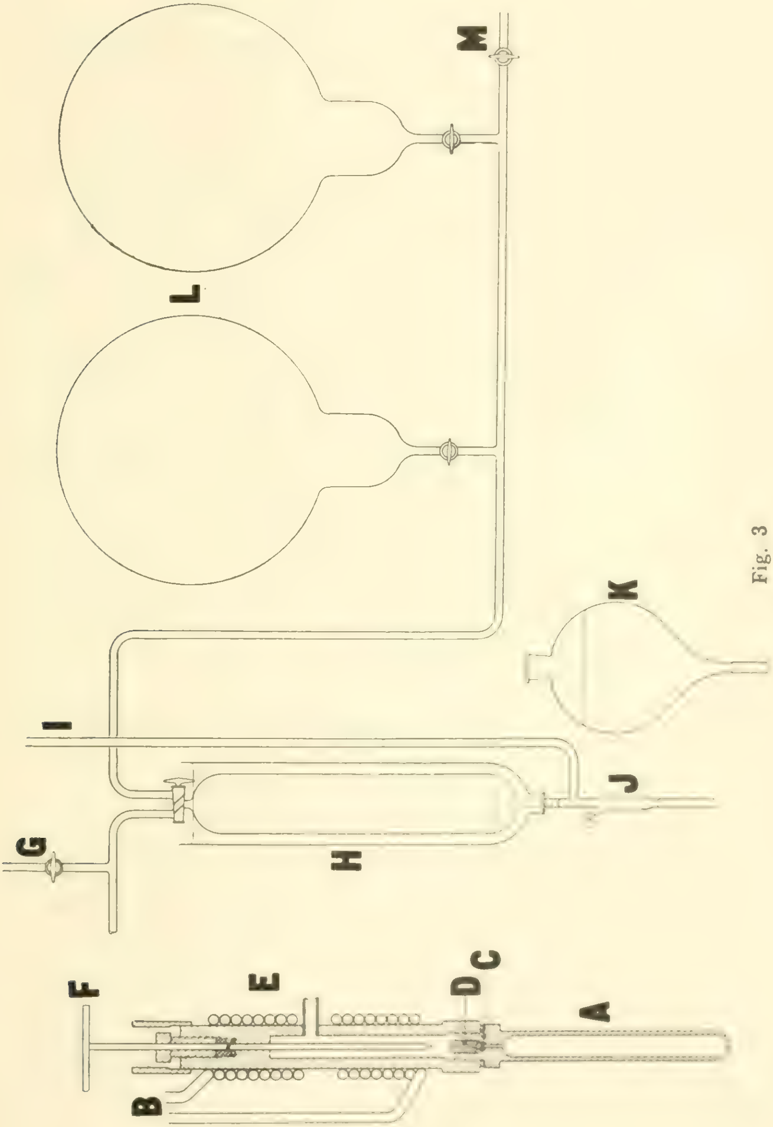

Fig. 3

of the piezometer was 7.6574 c.c. at zero to the under surface of the gold disk. The quantity of methane employed was about 0.17 to 0.19 g., corresponding to about 260 c.c. at N.T.P. and producing about 40 atms. in the piezometer at ordinary temperatures.

The procedure of loading consisted in first exhausting the burette H, connected by means of the two-way stopcock with the piezometer; the latter being, of course, heated to drive off adsorbed matter. Methane was then permitted to expand into H from the holders L and, when temperature equilibrium had been established, the pressure was read on the mercury column I. The burrette was of the constant volume type, with the lower burette mark engraved on a tube of the same diameter as the manometric tube, thereby avoiding capillary depression corrections. The quantity of methane in the burette was transferred to the piezometer by cooling the latter in liquid air and raising the mercury reservoir K, thus liquifying the methane in the piezometer. The piezometer was then locked by screwing down the screw D by means of the screw driver F. The methane remaining in the leads and in E above the gold disk was removed by means of a Toepler pump and the volume measured at a known temperature and pressure. To obtain the true mass requires the equation of state for methane or it suffices for the accuracy obtainable* to employ the weight of a liter at N.T.P. The weight of a liter taken as a mean of nine determinations by Baume and Perrot[9] is 0.7168 gram or 1394.2 c.c. N.T.P. per gram.

The loaded piezometer is connected with a piece of hexagonal steel carrying a 0.75 mm. bore steel tubing locking against an annealed aluminum washer, and placed inverted in the constant temperature bath. Referring again to Fig. 2, the piezometer with its steel tube can then be connected with the block C and the steel lead exhausted through V to the gold washer serving to confine the methane in the piezometer. After closing the stopcock in block C at V, mercury can be run in by screwing in the piston of the mercury volume injector G. It is to be added that a plug replaced the oil lead from I in D during the exhaustion and the oil lead was replaced after filling the block and lead with mercury. The oil lead having been connected, mercury is brought to the needle point* by manipulating the oil injector I and volume injector G. By this means a zero setting can be obtained at a definite pressure corresponding to the position of the mercury which is in contact with the gold disk closing the piezometer. After the zero setting is obtained the pressure is increased to several hundred atmospheres and in about twenty-four hours the gold disk, weakened by amalgamation with the mercury, is punctured, bringing the mercury into contact with the methane. By means of the mercury injector G a setting can be made for a chosen specific volume of methane and a series of pressures and temperatures observed.

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* The gas is measured in the burette H, Fig. 3, under other conditions of temperature and pressure than N. T. P., under which the liter is measured. Strictly, one should know the compressibility and coefficient of expansion of the gas to obtain the true weight of the actually measured quantity. The use of the perfect gas laws using the measured weight per liter leads to no appreciable error, however, in the case of methane, as was proved when the constants of the equation of state were obtained. It will be shown in the present paper that the weight of a liter of methane calculated by the equation of state agrees very well with the experimental determination of Baume and Perrot.

[9] Baume and Perrot, Jour. Chim. Phys. **7**, 1371, 1909.

It is necessary to know the temperature dilation of the mercury as well as its compressibility† while the stretch of the steel piezometer and apparatus can be obtained by separate blank measurements. For the true expansivity with temperature of the steel piezometer, the data of the Reichsanstalt were correlated as a function of the temperature as follows:

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* One of the difficulties encountered in the test series of measurements was the emulsification of the mercury at the needle point and junction of oil and mercury. This has the effect of making the contact uncertain and is due to the use of too high a voltage. It was to remedy this defect that the audion bulb system represented at E and T was introduced.

† The compressibility of mercury is a function of both pressure and temperature. Thus Bridgman gives the compressibility at one atmosphere as $3.80 \times 10^{-6}$ at 0° and $3.95 \times 10^{-6}$ at 22°. The decrease of the compressibility with pressure is given as about three per cent for the first thousand atmospheres. The effect of pressure increase may be neglected in the present work since 400 atmospheres were not exceeded. The temperature effect on the stretch of the piezometer is determined as the sum of that due to the compressibility of the mercury contained in the piezometer and the stretch of the piezometer itself. These direct measurements failed to disclose any pronounced effect on the combined mercury compressibility and piezometer stretch because of the small amount of mercury (7.6 c.c.) contained in the piezometer and the smallness of the temperature coefficient of stretch of the piezometer. The value $3.9 \times 10^{-6}$ was assumed for the mercury compressibility independent of the temperature. The total stretch of the piezometer amounted to $4.4 \times 10^{-5}$ c.c. per atm.

$$V_t^{Fe} = V_\circ(1+3.25\times10^{-5}t+2.85\times10^{-8}t^2-1.65\times10^{-11}t^3).$$

The equation for the volume of mercury as a function of the temperature as given by Callendar and Moss was employed.

$$V_t^{Hg} = V_\circ(1+1.80555\times10^{-4}t+1.2444\times10^{-8}t^2+2.539\times10^{-11}t^3)$$

## TABLE II

### Observed Pressure Represented as a Linear Function of the Temperature at Constant Volume.

| *Volume* | 0° | 50° | 100° | 150° | 200° | |
|---|---|---|---|---|---|---|
| | | | p = 0.16160T − 7.714 | | | |
| 35.104 | 36.37 | 44.55 | 52.63 | 60.70 | 68.66 | Pressure obs. |
| | 36.43 | 44.51 | 52.59 | 60.67 | 68.75 | Pressure calc. |
| | | | p = 0.19148T − 10.389 | | | |
| 30.089 | 41.89 | 51.55 | 61.17 | 70.68 | 80.09 | Pressure obs. |
| | 41.91 | 51.49 | 61.06 | 70.63 | 80.21 | Pressure calc. |
| | | | p = 0.23520T − 14.809 | | | |
| 25.075 | 49.21 | 61.20 | 72.96 | 84.64 | 96.22 | Pressure obs. |
| | 49.38 | 61.13 | 72.88 | 84.63 | 96.38 | Pressure calc. |
| | | | p = 0.30412T − 23.081 | | | |
| 20.059 | 59.85 | 75.35 | 90.56 | 105.63 | 120.42 | Pressure obs. |
| | 59.99 | 75.19 | 90.40 | 105.60 | 120.81 | Pressure calc. |
| | | | p = 0.42860T − 40.398 | | | |
| 15.045 | 76.47 | 98.34 | 119.88 | 140.95 | 161.76 | Pressure obs. |
| | 76.67 | 98.10 | 119.53 | 140.96 | 162.39 | Pressure calc. |
| | | | p = 0.71429T − 87.629 | | | |
| 10.030 | 107.25 | 143.66 | 179.61 | 214.59 | 250.03 | Pressure obs. |
| | 107.47 | 143.19 | 178.90 | 214.62 | 250.33 | Pressure calc. |
| | | | p = 0.81880T − 105.812 | | | |
| 9.026 | 117.08 | 159.21 | 200.51 | 240.62 | 280.55 | Pressure obs. |
| | 117.84 | 158.78 | 199.72 | 240.67 | 281.60 | Pressure calc. |
| | | | p = 0.96295T − 132.575 | | | |
| 8.024 | 129.73 | 179.03 | 227.58 | 275.10 | 321.92 | Pressure obs. |
| | 130.45 | 178.60 | 226.70 | 274.89 | 323.04 | Pressure calc. |

The shifting of the temperature requires, for preserving constancy of the methane volume, a resetting of the mercury injector G to compensate for the combined increase in volume of the mercury in the piezometer and the dilation of the piezometer with temperature and pressure. The method of making this computation, knowing the stretch of the piezometer and apparatus with pressure and the dilation of the piezometer and mercury with temperature, is obvious.

## The Experimental Data

The data were taken first at 50° continuing to 100°, 150° and 200°, making the observations, at zero, last in a Dewar tube filled with ice. In Table II will be found the absolute temperatures and pressures for the fixed volumes beginning with about 35 c.c. per gram of methane. A linear equation is given with each volume which has been used to calculate the pressures recorded under each observed pressure. It will be noted that the first and last observations are slightly higher than the observed values. This was finally traced to a slight but gradual drift in the compressibility of the packing of the stopcocks in the block C and that used to pack the piston in the mercury injector G. For this reason in making up the linear equation more weight was attached to the three middle sets of data at each specific volume.

The equation of state gives, for the tangent of the pressure-temperature lines at constant volume, the expression $\frac{R}{v-\delta}$. The magnitude of $R$ per mol is known with tolerable accuracy[10] being 82.058 $\frac{\textit{c.c., atm.}}{\textit{degrees C., mol.}}$. The molecular weight of methane has been

### TABLE III

**Values of δ Observed and Calculated by the Equation**

$$\log_{10}\delta = 0.56195 - \frac{1.05}{v}\ ;\quad \delta = 3.647e^{-\frac{2.42}{v}}$$

| *Spec. Vol.* | $\left(\frac{R}{v-\delta}\right)$ *obs.* | δ *obs.* | $\left(\frac{R}{v-\delta}\right)$ *calc.* | δ *calc.* |
|---|---|---|---|---|
| 35.104 | 0.16160 | 3.438 | 0.16143 | 3.404 |
| 30.089 | 0.19148 | 3.365 | 0.19149 | 3.366 |
| 25.074 | 0.23520 | 3.318 | 0.23514 | 3.312 |
| 20.059 | 0.30412 | 3.233 | 0.30413 | 3.233 |
| 15.045 | 0.42860 | 3.106 | 0.42861 | 3.106 |
| 10.030 | 0.71429 | 2.866 | 0.71418 | 2.866 |
| 9.026 | 0.81880 | 2.777 | 0.82054 | 2.790 |
| 8.024 | 0.96295 | 2.710 | 0.96099 | 2.699 |

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[10] Keyes, Jour. Am. Soc. Refrig. Eng. **8**, 505 1922.

## TABLE IV

Cohesive Pressure Term deduced for each Temperature from the Pressure-Temperature Tangent compared with the Cohesive Pressure calculated by means of Equation.

$$\phi = \frac{9802.2}{(v+0.565)^2}$$

| *Volume* | $\phi$ 0° | $\phi$ 50° | $\phi$ 100° | $\phi$ 150° | $\phi$ 200° | *mean* $\phi$ | *calc.* $\phi$ |
|---|---|---|---|---|---|---|---|
| 35.104 | 7.77 | 7.67 | 7.67 | 7.68 | 7.80 | 7.72 | 7.70 |
| 30.089 | 10.41 | 10.33 | 10.28 | 10.34 | 10.51 | 10.38 | 10.43 |
| 25.075 | 15.03 | 14.80 | 14.80 | 14.89 | 15.07 | 14.92 | 14.91 |
| 20.059 | 23.22 | 22.92 | 22.92 | 23.05 | 23.47 | 23.12 | 23.00 |
| 15.045 | 40.60 | 40.16 | 40.05 | 40.41 | 41.03 | 40.45 | 40.23 |
| 10.030 | 87.86 | 87.15 | 86.92 | 87.65 | 87.93 | 87.50 | 87.33 |
| 9.026 | 106.56 | 105.38 | 105.02 | 105.85 | 106.86 | 105.94 | 106.56 |
| 8.024 | 133.29 | 132.14 | 131.74 | 132.36 | 133.69 | 132.64 | 132.89 |

## TABLE V

Isometrics of Methane used to determine the Constants of the Equation of State. Pressures compared with those calculated by Equation of State.

$$p^{\text{atm.}} = \frac{5.1173}{v-\delta}T - \frac{9802.2}{(v+0.565)^2}; \quad \log_{10}\delta = 0.56195 - \frac{1.05}{v}.$$

| *Volume c.c./g* | 0° | 50° | 100° | 150° | 200° | |
|---|---|---|---|---|---|---|
| 38.104 | 36.37 | 44.55 | 52.63 | 60.70 | 68.66 | Pressure obs. |
| | 36.39 | 44.46 | 52.53 | 60.60 | 68.67 | Pressure calc. |
| 30.089 | 41.89 | 51.55 | 61.17 | 70.68 | 80.09 | Pressure obs. |
| | 41.87 | 51.45 | 61.02 | 70.59 | 80.17 | Pressure calc. |
| 25.074 | 49.21 | 61.20 | 72.96 | 84.64 | 96.22 | Pressure obs. |
| | 49.31 | 61.07 | 72.83 | 84.59 | 96.34 | Pressure calc. |
| 20.059 | 59.85 | 75.35 | 90.56 | 105.63 | 120.42 | Pressure obs. |
| | 60.07 | 75.28 | 90.48 | 105.70 | 120.90 | Pressure calc. |
| 15.045 | 76.47 | 98.34 | 119.88 | 140.95 | 161.76 | Pressure obs. |
| | 76.80 | 98.27 | 119.70 | 141.13 | 162.56 | Pressure calc. |
| 10.030 | 107.25 | 143.66 | 179.61 | 214.59 | 150.03 | Pressure obs. |
| | 107.74 | 143.45 | 179.16 | 214.86 | 150.57 | Pressure calc. |
| 9.026 | 117.08 | 159.21 | 200.51 | 240.62 | 280.55 | Pressure obs. |
| | 117.56 | 158.59 | 199.61 | 240.64 | 281.67 | Pressure calc. |
| 8.024 | 129.73 | 179.03 | 227.58 | 275.10 | 321.92 | Pressure obs. |
| | 129.59 | 177.64 | 225.69 | 273.74 | 321.79 | Pressure calc. |

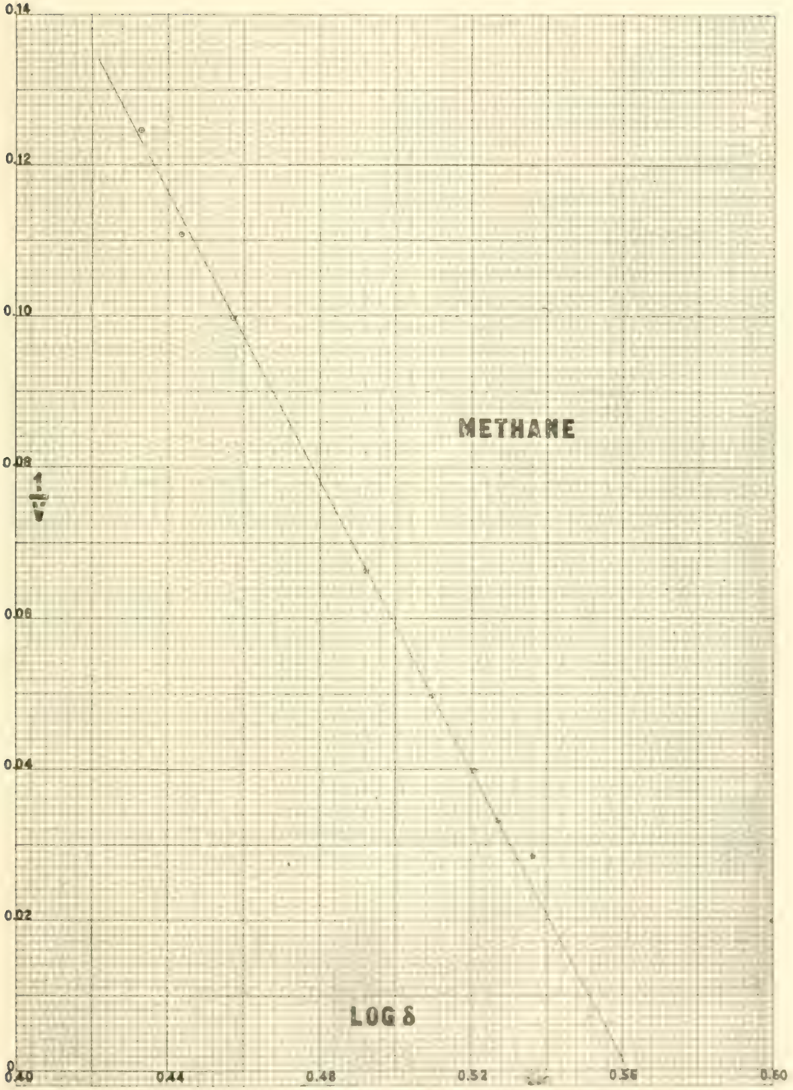
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0
$\frac{1}{v}$
METHANE
LOG δ
0.40
0.44
0.48
0.52
0.56
0.60

Fig. 4

taken as 16.035, using the atomic weights $H = 1.0075$ and $C = 12.005$. The value of $R$ per gram of methane is therefore 5.1173.

The values of $\delta$ may be calculated using the relation $\delta = v - \frac{R}{\left(\frac{\partial p}{\partial T}\right)_v}$ and since $\delta = \beta e^{-a/v}$ a plot can be prepared, using as coördinates log $\delta$ and $\frac{1}{v}\cdot$ The plot is reproduced in Fig. 4, showing that methane follows the function $\delta = \beta e^{-a/v}$. In Table III are listed the volumes per gram, the tangent obtained directly from the isometrics, the values of $\delta$ calculated from the tangents, the calculated tangents and $\delta$ values calculated by means of the $\delta$ equation accompanying the table.

To complete the equation of state it is necessary to obtain the constants of the cohesive pressure term $\phi = \frac{A}{(v+l)^2}\cdot$ For this purpose the values of the constants of the linear equations given in Table II may be used or the calculated tangent of each pressure-temperature datum may be used to deduce a corresponding $\phi$ value. For each volume this gives with the data of Table II five values of $\phi$ numerically identical except for errors in observation. Table IV gives, corresponding to each temperature, the value of $\phi$ obtained from the experimentally determined slope. The mean of these values is then calculated over to $\frac{1}{\sqrt{\phi}}\cdot$ which gives a straight line when plotted with $v$, as represented in Fig. 5. The equation heading the table has been used to compute $\phi$ "calculated." It is evident that the $\phi$ function represents the experimental data as well as could be expected. The complete equation of state for methane is, therefore:

$$p = \frac{5.1173}{v - \delta} T - \frac{9802.2}{(v + 0.565)^2}$$

$$\log_{10} \delta = 0.56195 - \frac{1.05}{v} \tag{1}$$

In Table V will be found the pressures calculated by means of equation (1) for comparison with the observed pressures.

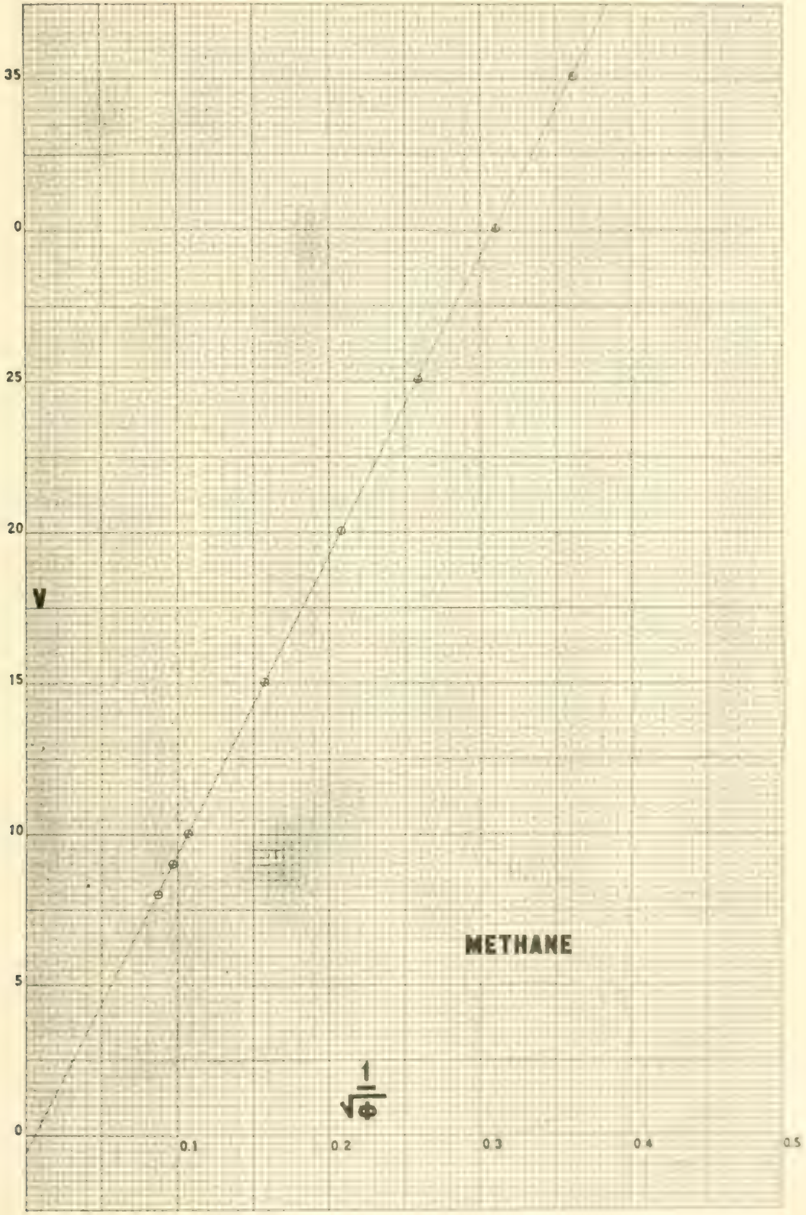

Fig. 5

This series of measurements, used to evaluate the constants of the equation of state, was made after studying the defects in the apparatus and introducing the amplifier circuit represented at D, E, T in Fig. 1. An earlier series obtained before the introduction of the latter is presented in Table Va, showing the disturbing effect of the emulsification of the mercury, due to the high voltage of the induction coil secondary used to excite the telephone on contact of the mercury with the needle point.

**TABLE Va**

**Series of Methane Isometrics obtained before Improved Mercury Contact Detector was employed. Pressures compared with those calculated by Equation of State.**

$$p=\frac{5.1173}{v-\delta}T-\frac{9802.2}{(v+0.565)^2}\ ;\ \log_{10}\delta=0.56195-\frac{1.05}{v}$$

| *Volume c.c./g* | 0° | 50° | 100° | 150° | 200° | |
|---|---|---|---|---|---|---|
| 37.394 | 34.35 | 42.00 | 49.51 | 56.98 | 64.49 | Pressure obs. |
| | 34.34 | 41.87 | 49.40 | 56.94 | 64.47 | Pressure calc. |
| 32.053 | 39.51 | 48.54 | 57.49 | 66.28 | 75.13 | Pressure obs. |
| | 39.53 | 48.55 | 57.37 | 66.30 | 75.22 | Pressure calc. |
| 26.710 | 46.56 | 57.71 | 68.59 | 79.30 | 90.17 | Pressure obs. |
| | 46.61 | 57.55 | 68.49 | 79.44 | 90.38 | Pressure calc. |
| 21.368 | 56.67 | 71.06 | 85.07 | 98.85 | 112.88 | Pressure obs. |
| | 56.80 | 70.93 | 85.06 | 99.18 | 113.31 | Pressure calc. |
| 16.026 | 72.63 | 92.74 | 112.41 | 131.55 | 151.19 | Pressure obs. |
| | 72.83 | 92.69 | 112.54 | 132.39 | 152.24 | Pressure calc. |
| 10.684 | 101.67 | 135.43 | 167.60 | 199.04 | 231.19 | Pressure obs. |
| | 102.31 | 135.22 | 168.13 | 201.04 | 233.95 | Pressure calc. |
| 9.615 | 110.76 | 149.42 | 186.22 | 222.24 | 258.90 | Pressure obs. |
| | 111.60 | 149.35 | 187.09 | 224.83 | 262.58 | Pressure calc. |
| 8.547 | 122.56 | 167.80 | 209.65 | 252.37 | 295.33 | Pressure obs. |
| | 123.06 | 167.19 | 211.33 | 255.47 | 299.61 | Pressure calc. |

The results of Amagat's measurements on the compressibility of methane are presented in the form of relative pressure volume products. By means of the equation of state, however, the ratio of the relative volume to the volume per gram may be found for one temperature and pressure. This factor will then serve as a means of comparing the Amagat observations with the present measurements or the equation of state. In Table VI, therefore, the volume corresponding to 39.5 atms. and 14.7° is 34.4 c.c./g., giving a factor of 1.899 relative volume units corresponding to 1 unit of c.c./g. The volumes at 131.6 and 263.2 atms. for 14.7° and 100° are computed using this factor, affording a basis for comparison with the volumes calculated by means of the equation of state at corresponding temperatures and pressures. Below 130 atms. the agreement is good, but Amagat's volumes are progressively larger as higher pressures are approached.

TABLE VI

**Comparisons of the Relative Volumes given by Amagat with the Volumes calculated at Corresponding Pressures and Temperatures by means of the Methane Equation of State.**

| Pressure | Temperature | | |
|---|---|---|---|
| Atm. | 14.7 | 100.1 | |
| 39.5 | $34.4 \frac{\text{c.c.}}{\text{g.}}$ | | Amagat |
| | $34.4 \frac{\text{c.c.}}{\text{g.}}$ | | Computed |
| 131.6 | 8.10 | 13.7 | Amagat |
| | 8.91 | 13.7 | Computed |
| 263.2 | 4.85 | 7.13 | Amagat |
| | 4.00 | 6.95 | Computed |

## Weight of a Liter of Methane at N.T.P.

Baume has most recently measured the normal density of methane[11]. A total of eleven determinations were made of which two were discarded in taking the mean. The extreme variation is 0.166 per cent in the nine values accepted, which give a mean of 0.7168 gram per liter N.T.P. Moissan and Chavanne[12] have also published a density, but only two determinations were made and conditions were not favorable for very exact work. The values relative to air are 0.5540 and 0.5554, showing a difference of 0.25 per cent.

[11] Baume, Jour. de Chim. Phys. **7**, 369, 1909.

[12] Moissan and Chavanne, C. r. **140**, 407, 1905.

The equation of state leads to the value 0.71718 gram per liter, which is one part in 1900 greater than 0.7168 obtained by Baume.

The coefficients of expansion at constant volume and constant pressure for one atmosphere have been published by Leduc[13]. The constant volume value is 0.003679 as compared with 0.0036796 by the equation of state. The constant pressure coefficient given by Leduc is 0.003681, while that computed is 0.0036834.

## SUMMARY

1. A new apparatus has been described for measuring the pressure-volume-temperature properties of a fluid by the "isometric" method. The particular piezometer employed is especially adapted for work with gases whose critical temperature lies well below zero.

2. The isometrics of methane have been measured and found to be linear within the limits of experimental error between zero and two hundred degrees up to three hundred atmospheres.

3. The equation of state has been found to represent the pressure-volume-temperature relation accurately. The following equation is for the units atm., c.c./g., degrees centigrade absolute.

$$p=\frac{4.1175}{v-\delta}T-\frac{9802}{(v+0.565)^2}$$

$$\log_{10}\delta=0.56195-\frac{1.05}{v}\cdot$$

4. The weight of a liter of methane calculated by means of the equation of state is 0.71718 as compared with 0.7168 given by Baume by direct measurement. The difference of one part in about nineteen hundred is well within the limits of experimental error of the Baume measurements.

5. The coefficients of temperature expansion at one atmosphere obtained from the equation of state are in agreement with the estimates independently made by Leduc.

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[13] Leduc, C. r. **148**, 1173, 1908.

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 148.)

# THE THERMODYNAMIC PROPERTIES OF METHANE

By Frederick G. Keyes, Robert S. Taylor and Leighton B. Smith

1. **Introduction. The Vapor Pressure of Methane.** There are very few published data for the vapor pressure of liquid methane. Olszewski's[1] results extend from the critical temperature to the freezing point, but the pressures are several atmospheres greater than the recent measurements of Cardoso[2] in the interval −84.4° to −97.0°. The critical pressure, for example, obtained by Olszewski is 54.9 atms. at a critical temperature given as −81.8° whereas Cardoso gives 45.60 atms. at −82.85°. No other measurements have been found in the literature.

In the case of methane there are two very material difficulties connected with securing accurate vapor pressure values. Thus it is necessary to maintain and measure temperatures from −80° to −180° and insure that the temperature readings lie on the absolute scale of temperature. The latter objective is by no means easy to insure, since the comparisons of secondary standard thermometers with the gas scale have not reached a stage where satisfactory concordance has been attained between various investigators. The relation of the platinum resistance thermometer to the gas scale, for example, has been shown by Henning[3] not to be the same below zero as above zero where the Callendar formula applies. In fact, no two of Henning's eight platinum resistance thermometers appeared to give identical readings at all temperatures below zero, although the $\delta$ constants of Callendar, obtained by using 0°, 100°, and 419.4° for some of the thermometers, were almost identical. The general inference was that the differences between the gas scale and the Callendar formula temperatures of the platinum resistance thermometers were very markedly affected by small variations in the temperature coefficient of the platinum wire.

[1] Olszewski, C. r. **100,** 940, 1885.

[2] Cardoso, Jour. de Chim. et Phys. **13,** 332, 1915.

[3] Henning, Ann. d. Phys. **40,** 635, 1913.

The further need in accurate low temperature work is a constant temperature bath whose temperature can be changed at will from zero to the lowest temperatures required. The use of liquids boiling under constant pressure for this purpose has been highly developed in the Leiden cryogenic laboratory of Professor Onnes, but is not as convenient as desirable owing to the necessity of changing the bath liquids for studies covering long temperature ranges. It is, in addition, necessary to vary and maintain constant the pressure over the boiling liquids. The device used by Henning in the paper referred to above consisted of a test tube, submerged in a bath of petroleum ether, into which liquid air is dropped as required. Evidently a bath of this description would be troublesome to use where observations are to be made requiring concentration of attention on the details of the physical measurements.

The purity of the methane to be used is of paramount importance. For the present work samples of the methane were employed prepared as described in the preceding paper on the equation of state of methane.

In view of the uncertain status of the behavior of the platinum resistance thermometer at low temperatures an investigation had already been made in the physics department laboratories of this Institute of the relation between the scales of the platinum resistance thermometers actually used in the present investigations with the gas scale. The freezing points of a number of substances lying between zero and the boiling point of oxygen were also measured in terms of the constant volume hydrogen gas scale to serve as calibration temperatures.

The question of the thermodynamic scale is of particular importance at low temperatures, since the effect of a given error in temperature measurements is of increasing significance as lower temperatures are approached. Thus for example, 0.1° at the ice point, 273.14, is an error somewhat greater than 1 per 3,000, whereas 0.1° at the boiling point of oxygen, 90.20, is of more than three times this magnitude. The temperatures recorded in the present paper are, then, those obtained by means of a platinum resistance thermometer compared directly with the constant volume hydrogen thermometer at a number of temperatures between zero and the normal boiling point of oxygen.

2. **Apparatus Details.** The apparatus of first importance is the cryostat represented to scale in Fig. 1. It consists of two pyrex Dewar tubes, one of which A serves to contain liquid air, or, under certain conditions, liquid ammonia. Support for the larger tube is provided by means of a brass ring encircling the flask and attached thereto are three brass strips screwed to the cast-iron base S. The cast-iron base also serves to carry the support rod for the motor H used to stir the contents of the bath itself. The inner Dewar tube is supported in the larger tube by means of an asbestos wood cover into which the smaller tube is cemented. The inner Dewar tube is provided with a cork support at its tip, from which a tube V leads to a source of hydrogen or to a vacuum.

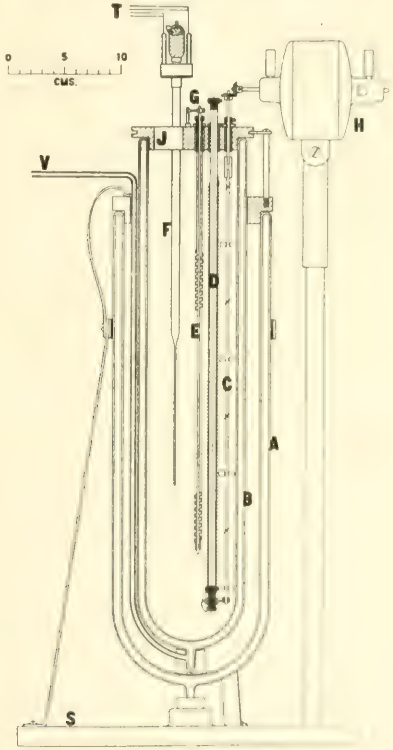

Fig. 1

The outer tube is silvered except for a rectangular strip which permits a view of the interior. The inner Dewar tube is supplied with a cover which serves as a support for the stirrer, heater, temperature regulator and platinum resistance thermometer. The cover of hard rubber is held firmly in place by three bolts carrying tongues of brass which fit into a slot turned into the periphery of the hard rubber cover. An opening is also provided at J for the introduction of the apparatus upon whose contents observations are to be made. It is, of course, essential that the introduction of heat by conduction should be a minimum and for this reason the stirrer rod C is interrupted by a hard rubber connector just under the cover. The shank of the thermometer is of monel metal turned to about 0.2 mm. thickness, and having the silver sheath containing the platinum wire silver-soldered thereto. The regulator consists of a 3 mm. width and 0.75 mm. thickness invar-brass thermostat metal.* This is wound in a helix as indicated and the upper end soldered to a thin brass tube. The lower end carries, floating, a fine monel rod passing loosely through a hard rubber bushing shown shaded at G. Here two platinum contacts are arranged and as the helix winds and unwinds, due to temperature changes, contact is made and broken. The sensitivity is limited by the pressure necessary to make electrical contact. The maximum sensitiveness which has thus far been attained at the lower temperatures is about 0.1°. The platinum resistance thermometer, however, indicating 0.001° makes it easy to secure a temperature constant to 0.01°. The combination of hand regulation with the automatic requires an operator to watch the galvanometer of the resistance bridge and manipulate resistances in accordance with the deflections of the galvanometer. The bimetallic helix, on the other hand, would have great sensitivity were it not for the really considerable pressure needed for good electrical contact. It is hoped that in time means for surmounting the latter difficulty will be evolved, since it is most convenient to have the bath automatically regulated.

The heater consists of a very thin steel, or preferably monel, tube upon which is wound the resistance wire over thin mica.

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* This excellent material was obtained in several thicknesses and lengths through the kindness of the H. A. Wilson Co. of Newark, N. J.

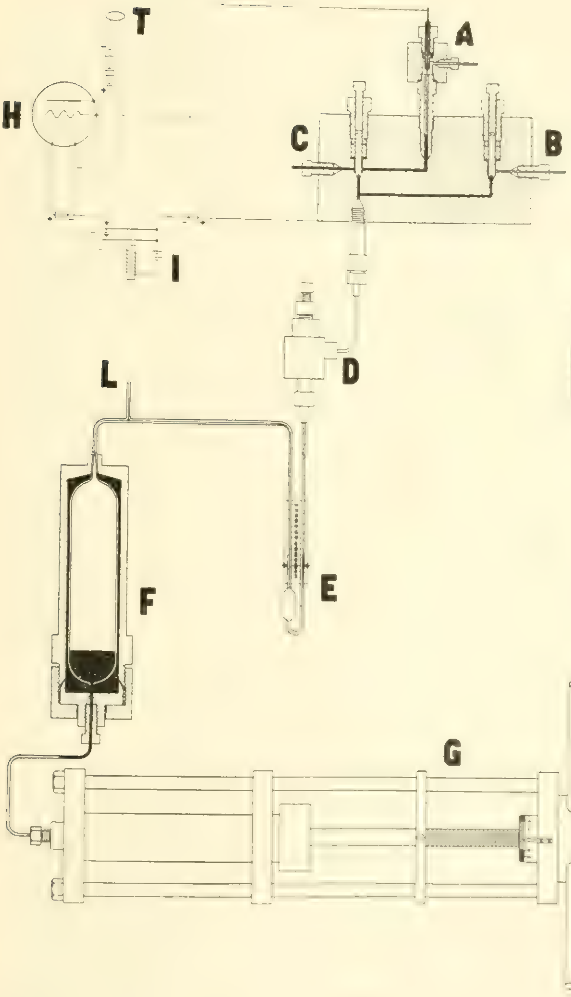

Fig. 2

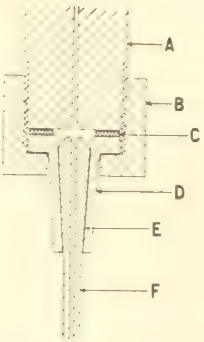

Fig. 2a

Talc plugs serve to insulate the free end of the wire which passes through the center of the supporting tube.

The method of operating the bath consists in adjusting the pressure of hydrogen in the interspace of the Dewar tube B until sufficient cooling of the bath fluid is secured to balance the mean value of the heating current. For the lowest temperatures, for example, as good as possible conductivity of the interspace is required and a centimeter pressure of hydrogen is sufficient. At high temperatures, on the other hand, a relatively low pressure is necessary on account of the greater difference in temperature between the contents of the cryostat bath B and the surrounding liquid air. For temperatures above −30° it is best to use liquid ammonia in the outer dewar tube, and thus any temperature in the range between 0° and −180° may be easily established and maintained.

The vapor pressures were measured in two separate pieces of apparatus. Pressures above several atmospheres were measured at the time the densities of the liquid were being measured, while a special apparatus was used for the lower pressures down to the triple point. In Fig. 2 is represented the block C as described in the preceding paper on the equation of state for methane. A is the mercury oil contact, the oil lead connecting with the piston pressure gauge. C leads to the mercury volume-measuring injector and B leads to the vacuum pump. The electrical circuit for indicating mercury contact at the oil junction within A consists of an audion bulb, induction coil primary, dry batteries and telephone.

The steel stopcock D serves to shut off the mercury in the pyrex glass volume-measuring apparatus* E, which connects by

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* The coefficient of temperature expansion of pyrex glass has not been measured at low temperatures. The following equation for the true volume at any temperature $t$ is based on the mean expansion measurements in a weight-thermometer of pyrex glass between 0 and 100, and 100 and 218°.

$$V_t^{\text{pyrex glass}} = V_\circ (1 + 9.68 \times 10^{-6} t + 3.11 \times 10^{-9} t^2)$$

The error that extrapolation to −180° may introduce in the measurements of the specific volume of liquid methane is inconsiderable unless the coefficient of expansion of pyrex glass is widely different from soda glass in its general expansion behavior. This is not inferred since its expansion properties are quite similar to soda and other glasses above zero.

The expansion of the volumenometer with pressure was determined at zero degrees by blank measurements with the bell F sealed off from the

0.75 mm. bore pyrex glass tubing at one side with the steel cock** D and at the other with the pyrex glass bell (2.75 cm. diameter and 12.5 cm. long) enclosed in the steel case F. The capillary lead L is used to exhaust the glass portion previous to the introduction of the methane. The compressor G connecting with F serves to force methane into E where the liquid volumes were measured. It is perceived that the apparatus consists of a constant volume portion E, which can be filled with liquid methane at any temperature in the liquid region by manipulating the mercury injector G transferring methane from the reservoir F at ordinary temperatures.

The volume of E (1.5798 c.c. at 0°) together with the capillary leads was determined by filling with mercury and weighing. The volume of the bell within F (about 75 c.c.) was measured by means of the piston G. The injector G (total volume capacity 56 c.c.) was calibrated by weighing the mercury ejected for each five turns of the nut advancing the piston. The position of the piston was indicated by a "cyclometer" giving the number of whole turns, and the fractions of a turn, on the nut whose periphery was divided into one hundred divisions. The piston was so adjusted that practically at its maximum inward travel the mercury stood at a mark on the capillary of determined volume per unit length above F. The glass bell was, of course, so

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volumenometer. Correction could, therefore, be made for the stretch of E with pressure although this was not determined as a function of the temperature. Previous experience with soda glass above zero has shown that the temperature coefficient of the pressure stretch is very small within the elastic limits of the glass.

**In Fig. 2a is represented an enlarged drawing of the method employed to connect the steel and glass. The glass capillary F is thickened to an inverted cone shape and ground to fit the steel piece D. The member D is then warmed and a thin layer of a cement made from shellac which has been digested on a water-bath with fifteen per cent of North Carolina oil of tar, is wiped over the ground surface. The glass member is now seated in the steel part D, turning the glass member in its seating position until the cement is squeezed out and the ground surfaces in as close contact as possible. Connection can now be made with any other part of the steel apparatus, as represented at A, by means of a union B, using an annealed aluminum disk C. The glass capillary F should be joined *in situ* to the remaining portion of the glass apparatus to avoid strains at the rigid steel construction. The joint of the steel and glass bell F is made in the same manner as described. The joints described are vacuum tight, resist the action of mercury and hold against pressure to the limit of the glass. They cannot be used, however, above 100°.

proportioned (75 c.c. capacity) that when the piston was withdrawn to the complete outward travel of the screw, mercury sealed the lower end of the bell. Methane from the storage globe was now passed over into a measuring burette, similar to the one used in loading the piezometer employed in measuring the isometrics of the gas phase, and condensed finally in E at the temperature of liquid oxygen. The capillary lead at L was then sealed and the gas remaining in the leads between L and the measuring burette pumped off and measured. Before E was allowed to warm to room temperature the mercury was lowered in F to the maximum by withdrawing the piston of G. The methane could then be safely allowed to evaporate from E, filling a space of about 56 c.c. and producing a total pressure of only 10 atms. at ordinary temperatures.

To make a measurement of the specific volume the volumenometer E was brought into the cryostat already described. A glass scale divided into millimeters was placed back of the volumenometer serving to give indication of the position of the level of the meniscus of liquid methane relative to two etched marks on the capillary extensions from the volumenometer bulb. At a fixed temperature mercury was forced over from a second mercury injector communicating from B until the meniscus was just about at the level of the cover of the cryostat and fixed in position by closing the steel stopcock D. By means of G methane was forced to condense in E until the liquid methane menisci were about at the two etched marks on the volumenometer stems. A fixed volume of liquid methane was, therefore, confined by the gas phase present in the capillary leads. The total mass of methane was known after sealing at L and the volume, temperature and pressure of the methane existing in the gas phase, from the reading of the position of the piston of the injector G and the volume of the glass capillary tubing. By means of the equation of state the mass of this known total gaseous volume could be computed, and the mass of the liquid methane of known volume in E deduced. Before changing the temperature of the cryostat the steel cock D could be opened and an observation made of the vapor pressure. In this manner practically the whole temperature range of the existence of the liquid phase could be measured. The critical temperature was ascertained and also the critical pressure.

In the procedure described no mention has been made of the influence of adsorption in removing methane from the phase under observation. The volumenometer E was exhausted at 360° for several hours previous to admitting the methane. No certainty is afforded that adsorption did not take place, but freeing the glass surface from adsorbed moisture appears, from general experience, to minimize the adsorption of the permanent gases.* The bell F could not be evacuated hot, so that no certain knowledge is available as to the amount of methane adsorbed. The total mass of methane was, however, sufficiently large, so that, if ten molecular layers of methane were adsorbed, the effect would scarcely be detectable with the accuracy attainable in the volumenometer measurements.

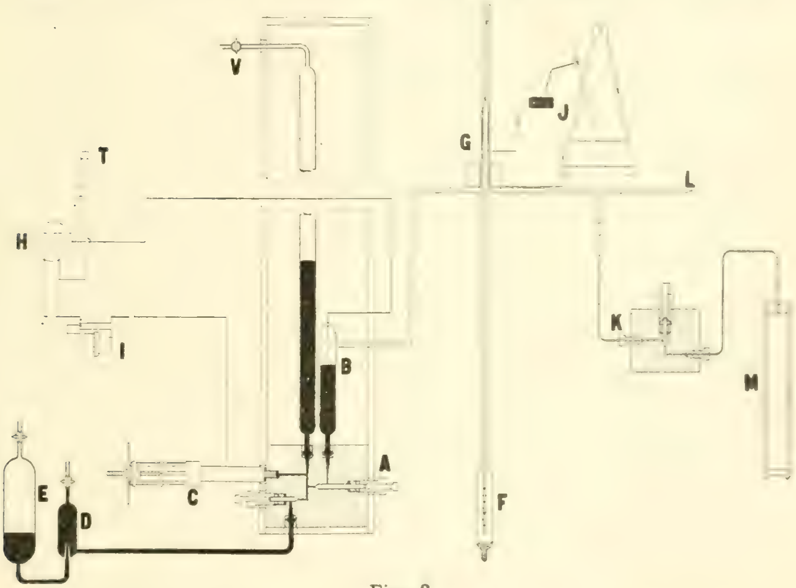

Fig. 3

The measurements of saturation pressure below several atmospheres were carried out in a special apparatus, since the piston gauge is not suitable for low-pressure measurements. The general apparatus is represented in Fig. 3. The manometer tubes were selected of uniform bore, 1.5 cm. in outside diameter and the actual diameter along the length determined by weighing mercury taken from successive intervals along the length of the longer leg. The short leg of the manometer was provided with a finely pointed platinum wire sealed into the closed end and the diameter accurately determined at the section in the plane of the point. With the true tube diameters a table was then computed giving the correction for capillary depression for different heights of mercury. The corrections for capillary depression with tubing 1.5 cm. I.D. will rarely exceed a few hundredths mm. with tubes of moderate uniformity of bore. Each manometer tube was ground to a seat in the steel block A* having steel cocks to cut off the two legs of the manometer and the levelling reservoir E. The mercury in the reservoir E was passed through the trap D to prevent air from gaining access to the manometer tubes, and all connections were of glass. Compressed air and vacuum served to manipulate the entrance and exit of mercury to the manometer, while fine adjustment was secured by means of the mercury piston injector C. The purpose of the platinum contact B in the short arm was to aid in observing equilibrium of the methane in the container F and to save continually reading the mercury level in the short arm, since the reading of the level when contact just makes is reproducible to the limit of sensitiveness of the cathetometer (0.02 mm.).

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* It was shown by Eumorphopoulos (Proc. Roy. Soc. 90 A, 189, 1914) that only by repeatedly heating and rinsing with dry nitrogen could the coefficient of volume increase with temperature at constant pressure be made reproducible. Isometric measurements with ammonia in this laboratory have indicated that adsorption is greatly minimized by long baking out of the glass at the best vacuum obtainable.

The methane container during the actual measurements consisted of the tube F containing an electro-magnetically operated glass stirrer as indicated. The coil G was energized periodically by means of the metronome contacting device represented. It is, of course, necessary to adjust the period of the metronome to the elastic characteristics of the spring by which the stirrer is suspended. The soft iron rod constituting the armature is enclosed in glass just below the eye used to fasten the lower end of the spring.

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* The ground joints and block were warmed and set with the shellac cement, as described in the case of the steel-glass joint represented in Fig. 2. An enlarged and threaded portion was produced in the steel block above the ground cone, for the purpose of preventing the tubes floating off their seat. The tubes themselves were enlarged, as indicated, at a point where they would come within the threaded part and at the time of seating the tubes, when both glass and steel were hot, cement was poured into the threaded cavity. With the construction here indicated the glass cones can be made and ground so that the bore of the glass coincides with the communicating hole in the steel, eliminating thereby any tendency to trap gas.

The exhaustion of the apparatus took place through the lead at L, while the long leg of the manometer was exhausted or exposed to the atmosphere at V depending on the magnitude of the pressure to be measured. The methane to be used in the measurements was transferred from the glass storage globes to the steel tube container M provided with a steel block carrying a cock and lead K. Methane was condensed in M by means of liquid air, after having been thoroughly exhausted. Connection was made to the glass apparatus by means of the shellac cement. When the entire apparatus was thoroughly exhausted to the cock in the steel block K, the tube F was brought into the cryostat, adjusted to the lowest temperature (−180°), and by opening the cock of the steel methane container, a quantity of methane was condensed in F for the measurement of the vapor pressure. The exhausting lead L carried a stopcock in order to permit of pumping the methane between successive measurements, thus insuring the absence of foreign gas, although the methane during its introduction into the container M was treated to remove all permanent gases. At the conclusion of a day's measurements, the methane could be transferred from the tube F to the container M and held under pressure for future measurements.

3. **The Temperature Measurements.** The temperatures recorded should lie on the absolute or thermodynamic scale and, while numerous investigations have resulted in fixing with considerable certainty the thermodynamic scale above zero, the temperature scale below zero, as already stated, is by no means as completely investigated. The difficulties, indeed, are increased in the region below zero, due to the difficulties of refrigeration, lack of convenient cryostats and errors introduced in the gas thermometry by adsorptive effects. The latter are of increasing significance as the temperature is lowered and are, moreover, par-

ticularly difficult to investigate quantitatively. Unfortunately, as Henning has shown, the platinum resistance thermometer does not follow the Callendar formula in its relation to the thermodynamic scale below zero. Moreover, owing to the fact that the wire contracts on cooling, it is not easy to devise a method of winding which will avoid the production of strains. Above zero, on the other hand, the wire expands and the tension of the wire on its support is relieved.

Owing to the importance of an accurate knowledge of the true temperature indications of the particular platinum thermometer employed in the present work, an extended comparison was made directly with the constant volume hydrogen thermometer employed in an investigation of the low temperature scale by Keyes, Townshend and Young in this Institute. The actual curve, (Fig. 14 of their paper), shows the difference between the Callendar formula platinum resistance thermometer temperatures and those of the quartz hydrogen thermometer of constant volume. The hydrogen gas scale temperature of the boiling point of pure oxygen at 76 cm. was found to be $-182.94$ as compared with $-182.93$ of Onnes[4] and $-182.97$ of Henning.[5] The boiling point of carbon dioxide at 76 cm. was similarly found to be $-78.53$ as compared with $-78.52$ found by Henning.[5]

4. **The Vapor Pressure Measurements.** The measurements at higher pressures made in the apparatus represented in Fig. 2 extend from about 4.5 atms. at 133.6° abs. to the critical temperature 191.03°. The low pressure measurements extend from about 7.5 degrees above the triple point[6] temperature to about 114.6°.

The higher pressure measurements consist of two series presented in Table I. The low pressures were measured in a small cryostat whose diameter (6.7 cm.) was small compared with the length (30 cm.). Efficiency of stirring of the bath fluid of propane and butane is necessary before the experimental tube can be assumed to be at the same temperature as the thermometer.

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[4] Onnes and Braak, Leiden Comm. No. 107a, 1908.

[5] Henning, Ann. d. Phy. **43,** 289, 1914.

[6] Crommelin, Com. Leiden Phys. Lab. No. 131, 1912. The temperature of the triple point is given as $-183.15$ and the pressure 7.0 cm.

## TABLE I

### Methane Vapor Pressures

| | Series 1 | | | Series 2 | |
|---|---|---|---|---|---|
| *Temperature Abs.* | *Observed Pressure Atms.* | *Calc. Pressure Atms.* | *Temperature Abs.* | *Observed Pressure Atms.* | *Calc. Pressure Atms.* |
| 133.628 | 4.514 | 4.493 | 143.380 | 7.574 | 7.515 |
| 138.558 | 5.874 | 5.880 | 158.549 | 14.634 | 14.839 |
| 143.495 | 7.590 | 7.558 | 168.267 | 21.737 | 21.637 |
| 148.439 | 9.579 | 9.565 | 168.351 | 21.707 | 21.704 |
| 153.385 | 11.949 | 11.936 | 172.355 | 25.004 | 25.073 |
| 158.339 | 14.639 | 14.711 | 178.189 | 30.500 | 30.626 |
| 163.295 | 17.897 | 17.928 | 181.203 | 33.684 | 33.812 |
| 172.437 | 25.146 | 25.146 | 186.084 | 39.626 | 39.449 |
| 178.189 | 30.486 | 30.626 | 186.147 | 39.389 | 39.525 |
| 181.203 | 33.700 | 33.812 | 188.005 | 41.807 | 41.835 |
| 186.147 | 39.511 | 39.525 | 189.931 | 44.207 | 44.326 |
| | | | 191.031 Crit. | 46.063 | 45.792 |

## TABLE II

### Low Vapor Pressure Measurements of Methane

| *T* | *Series 1 Pressures Atms.* | *Series 2* | *Series 3* | *Series 4* | *Series 5* | *Series 6* | *Mean of Series* 4, 5, 6 | *Pressure Calc. by Equation* |
|---|---|---|---|---|---|---|---|---|
| 97.293 | 0.2638 | 0.2625 | 0.2620 | 0.2575 | 0.2575 | 0.2571 | 0.2574 | 0.2574 |
| 100.902 | 0.3855 | 0.3847 | 0.3815 | 0.3774 | 0.3785 | 0.3781 | 0.3780 | 0.3780 |
| 106.003 | 0.6276 | 0.6271 | 0.6228 | 0.6216 | 0.6210 | 0.6197 | 0.6208 | 0.6196 |
| 110.023 | 0.8925 | 0.8928 | 0.8858 | 0.8839 | 0.8852 | 0.8829 | 0.8840 | 0.8830 |
| 114.631 | 1.2917 | 1.2903 | 1.2860 | 1.2846 | | 1.2812 | 1.2829 | 1.2823 |

Table II gives the low pressure series. The resistance bridge, in each series of measurements, made at different times, was brought to the same indication and the bath regulated at the corresponding temperature. In this manner the various changes in the external conditions affecting the measurements could be investigated. It was found necessary to increase the speed of the stirring of the bath markedly to secure constancy of the vapor pressure and also the agitation of the liquid methane by means of the electro-magnetic stirrer. To establish the absence of hydrogen or air the vapor phase of the methane could be pumped off from time to time during the measurements, and at the conclusion of the day's run from the frozen methane in the steel container before closing the steel cock K. The three final series 4, 5, and 6 show equilibrium was attained and these values have been used to form the mean pressure upon which the equation for the vapor pressure as a function of the temperature was based.

Some disappointment was felt that the measurements at higher pressures presented in Table 1 were not more concordant. This is not due to any lack of sensitiveness in the pressure-measuring device or lack of constancy in the temperature of the cryostat. It is believed to be due possibly to lack of sufficient stirring or agitation of the liquid methane under measurement. The construction of the apparatus and the purpose it had to serve precluded an effective stirring device, but a form of stirrer is being perfected which may permit the full utilization of the sensitiveness of the present pressure-measuring apparatus.

The equation used to relate the pressure to the temperature is of the form employed for ammonia and carbon dioxide.

$$\log p = -\frac{a}{T} + m + bT + cT^2 + dT^3 + \ldots \qquad (1)$$

The evaluation of the constants of this equation can sometimes, as was illustrated in the case of ammonia and carbon-dioxide, be best attained by using the equation in the "critical-constants" form:[7]

$$\log p = -\frac{Z\,(T_c - T)^2 + \omega}{T} + m \qquad (2)$$

In the case of methane, however, it was found to be preferable to select the approximate equation $\log p = -\frac{a'}{T} + m'$ and, by comparing the calculated with the observed logarithms of the pressures, obtain values designated as

$$\Delta \log p = \log p \text{ obs.} - \log p \text{ calc.}$$

These values were then plotted with the reciprocal of the corresponding absolute temperatures and the best curve drawn to represent the final relation. The curve was then represented by means of the equation.

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[7] Thermodynamic Properties of Ammonia. Keyes and Brownlee, Wiley & Sons, page 10, 1916.

$$\Delta \log p = -\frac{\Delta a}{T} + \Delta m + bT + cT^2 + dT^3$$

where $\Delta a$ and $\Delta m$ are constants which can be used in comparing with the approximate equation to give the final equation for log $p$ as a function of the absolute temperature. The final equation is as follows where $T = (t + 273.13)$

$$\log_{10} p^{\text{atm.}} = -\frac{595.546}{T} + 8.09938 - 4.04175\times10^{-2}T + 1.68655\times10^{-4}T^2 - 2.51715\times10^{-7}T^3 \qquad (3)$$

**TABLE III**

**Methane Vapor Pressure Data**

| *Temperature Deg. Abs.* | *Vapor Pressure Calc. Atms.* | *Temperature Deg. Abs.* | *Vapor Pressure Calc. Atms.* | *Temperature Deg. Abs.* | *Vapor Pressure Calc. Atms.* |
|---|---|---|---|---|---|
| 95.00 | 0.1982 | 125.00 | 2.670 | 160.00 | 15.74 |
| 100.00 | 0.3444 | 130.00 | 3.641 | 165.00 | 19.14 |
| 105.00 | 0.5646 | 135.00 | 4.853 | 170.00 | 23.05 |
| 110.00 | 0.8813 | 140.00 | 6.338 | 175.00 | 27.49 |
| 111.52 | 1.0000 | 145.00 | 8.132 | 180.00 | 32.51 |
| 115.00 | 1.319 | 150.00 | 10.27 | 185.00 | 38.15 |
| 120.00 | 1.905 | 155.00 | 12.79 | 190.00 | 44.42 |
| | | | | 191.03 Crit. | 45.79 |

In Table III will be found the vapor pressures in atmospheres for each five degrees beginning with 95° abs. and ending with the critical pressure. The critical temperature and pressure were directly observed and may be compared with the value given by Cardoso* of —82.°85, as compared with —82.°10 obtained in the present investigation.

Cardoso worked under great difficulties in connection with his thermometry and exercised the greatest care and skill in the construction of his pentane thermometers. Difficulties were encountered also in connection with the lag in the expansion and contraction of the glass comprising the thermometers, so that in spite of all the precautions taken errors of temperature were difficult to avoid.

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* Cardoso, Jour. de Chim. Phys. **13,** 332, 1915.

In Table IV will be found the pressures given by Cardoso at the temperature observed with his pentane thermometer. The pressure measurements were made with a closed manometer, using the usual precautions to insure accuracy. It will be noted in the table that the Cardoso pressures are uniformly higher than those calculated by the Equation (3) and that the differences in temperature corresponding thereto are roughly the same order of magnitude, except the datum at 176.14°. The average temperature difference amounts to 0.56° and this correction applied to Cardoso's temperatures would bring the corresponding pressures into fair accord with the present measurements.* It will be noted in the

**TABLE IV**
**Cardoso Vapor Pressure Data**

| $T$ | 188.74 | 187.54 | 185.14 | 182.14 | 178.14 | 176.14 |
|---|---|---|---|---|---|---|
| $p^{\text{atms.}}_{\text{Cardoso}}$ | 43.85 | 42.03 | 38.88 | 35.40 | 31.00 | 29.40 |
| $p^{\text{atms.}}_{\text{cal.}}$ | 43.226 | 41.242 | 38.312 | 34.847 | 30.577 | 28.586 |
| $\Delta p$ | .624 | .788 | .568 | .553 | .422 | .814 |
| $\Delta T$ | .49 | .63 | .48 | .49 | .42 | .84 |

Mean $\Delta T = 0.56$

Correcting $T$ crit. of Cardoso gives $-82.29$
$T$ crit. M. I. T. $-82.11$
Olszewski 1885 $-81.8$

$p$ crit. Cardoso 45.6 atms. $\pm 0.1$
$p$ crit. M. I. T. 45.8 atms.

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* Cardoso, in verifying the readings of his pentane thermometer, used the freezing point of toluene, accepting a value for the freezing point, due to Timmermans, in 1912, of $-94.5$. In this laboratory, there has been found for pure toluene $-95.70$ referred to the $H_2$ constant volume scale. Recently Timmermans, Van der Horst and Onnes (Chem. Ab. June 10, p. 1694, 1922) give $-95.1$.

table that the critical pressure given by Cardoso is in good agreement with the pressure observed in this investigation. The temperature of the critical condition would, of course, be independent of any thermometer and a correction of 0.56 applied to the critical temperature, as observed with the pentane thermometer, would give −82.29, which is not in bad agreement with −82.11 obtained in these measurements, since the temperature of the critical phenomenon is difficult to locate exactly and, moreover Cardoso has shown that it is best to stir the liquid in observing the critical temperature, whereas in this work no stirring was employed. In the section wherein the densities of liquid methane are presented it will be shown that a correction of about 0.6° in Cardoso's temperature brings his densities into good agreement with the new values.

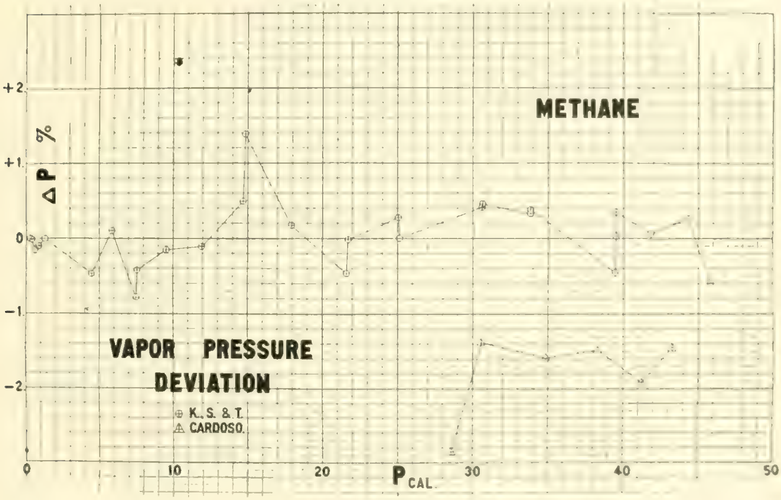

Fig. 4

In Fig. 4 the deviations of the individual pressure measurements of Tables 1 and 2 from the pressures calculated by means of Equation (3) are presented. The results obtained by Cardoso have been also inserted. It is evident that Equation (3) represents the new measurements as satisfactorily as can be expected.

5. **The Specific Volumes of the Liquid and Vapor Phases.** The apparatus, Fig. 2, used to measure the liquid specific volumes has already been described in connection with the vapor pressures. The method is of general applicability for the measurement of the liquid specific volumes for all substances whose critical temperature lies below the freezing point of mercury. The procedure, however, of confining the liquid in the volumenometer E by means of the gas phase requires that the mass of fluid in the gas phase, including that portion in the reservoir F, be determinable from a knowledge of its pressure, volume and temperature. This requirement has been met, in the present instance, from a knowledge of the methane equation of state, but empirical use of the experimental isotherms of gaseous methane could also be made.

The volume of the volumenometer between the engraved marks on the capillaries was 1.5798 cc., while the used volume of the reservoir was about 56 cc. The total quantity of methane employed amounted to about 0.66 g. to 0.78 g., most of which would reside in the volumenometer at the lowest temperatures, but in the bell F at the highest. Owing to the relatively large fraction of the total mass of methane being contained in the reservoir and in the capillary leads of the volumenometer, the accuracy of the specific volume measurements becomes rapidly impaired near the critical temperature. Measurements, however, were carried out to 190.38 or within about 0.65 degree of the critical temperature. The latter temperature was observed directly, but the reliability of the observation would have been much enhanced by stirring the fluid, as has been pointed out in particular by Cardoso.

The actual density measurements for the two series of measurements are presented in Table V. For the greater part two observations at the same temperature setting were made at different times, which give a means of judging of the reproducibility of the method. It will be observed that the concordance is satisfactory on the whole, although in some instances (181.20°, Series A) a large difference (one part in 230) occurs. On the average, however, one part in fifteen hundred or better is attainable in individual measurements. The entire range of the liquid phase has been practically covered and the " smoothed values " are those obtained

## TABLE V

### Methane Liquid Densities

| Series A | | | Series B | | |
|---|---|---|---|---|---|
| *Temperature Deg. Abs.* | *Density Liquid gm./c.c. Obs.* | *Density Liquid gm./c.c. Smoothed* | *Temperature Deg. Abs.* | *Density Liquid gm./c.c. Obs.* | *Density Liquid gm./c.c. Smoothed* |
| 186.143 | .2505 | .2504 | 128.562 | .3980 | .3989 |
| 186.143 | .2504 | .2504 | 128.562 | .3979 | .3989 |
| 181.203 | .2768 | .2762 | 123.911 | .4051 | .4059 |
| 181.203 | .2756 | .2762 | 123.911 | .4049 | .4059 |
| 178.189 | .2882 | .2881 | 119.249 | .4129 | .4128 |
| 178.189 | .2879 | .2881 | 119.249 | .4127 | .4128 |
| 172.437 | .3067 | .3067 | 114.631 | .4196 | .4196 |
| 172.437 | .3067 | .3067 | 114.631 | .4195 | .4196 |
| 168.351 | .3186 | .3182 | 110.023 | .4266 | .4263 |
| 168.351 | .3185 | .3182 | 110.023 | .4262 | .4263 |
| 163.295 | .3312 | .3312 | 106.003 | .4313 | .4321 |
| 163.295 | .3313 | .3312 | 105.451 | .4329 | .4329 |
| 158.339 | .3429 | .3429 | 100.903 | .4394 | .4394 |
| 158.339 | .3426 | .3429 | 153.193 | .3542 | .3544 |
| 153.385 | .3531 | .3540 | 158.171 | .3439 | .3433 |
| 153.385 | .3531 | .3540 | 181.100 | .2768 | .2766 |
| 148.439 | .3631 | .3644 | 186.054 | .2510 | .2509 |
| 143.495 | .3752 | .3741 | 187.974 | .2366 | .2375 |
| 143.495 | .3750 | .3741 | 188.937 | .2279 | |
| 138.558 | .3828 | .3829 | 189.902 | .2170 | |
| 138.558 | .3832 | .3829 | 190.381 | .2093 | |
| 133.628 | .3907 | .3910 | | | |
| 133.628 | .3909 | .3910 | | | |
| 128.704 | .3985 | .3987 | | | |
| 128.704 | .4000 | .3987 | | | |

by plotting the densities rather than the specific volumes. Two densities at the extreme temperature ends of the liquid phase were chosen, and a linear equation determined from which deviations of each observed datum could be computed. By plotting these deviations with the corresponding temperatures a smooth curve could be drawn, from which the values tabulated as smoothed were read. The device is evidently equivalent to the construction of a very large plot of the observed data.

There have been found in the literature only the data of Cardoso already briefly referred to in the section dealing with the vapor pressure. It was pointed out in the latter section that the temperatures recorded by Cardoso appeared by comparison of the

**TABLE VI**

**The Cardoso Saturation Specific Volumes**

| $T$ | $V_1$ Cardoso | $V_2$ Cardoso | $V_1$ M.I.T. from Mean Dens. Equa. | $V_2$ M.I.T. | Cardoso $V_1$ Corr. | Cardoso $V_2$ Corr. |
|---|---|---|---|---|---|---|
| 166.1 | 32.05 | 3.085 | 32.85 | 3.076 | 32.92 | 3.071 |
| 173.1 | 23.20 | 3.307 | 23.75 | 3.280 | 23.80 | 3.288 |
| 178.1 | 18.80 | 3.500 | 19.02 | 3.465 | 19.29 | 3.476 |
| 179.1 | 17.18 | 3.559 | 18.15 | 3.510 | 17.65 | 3.532 |
| 183.1 | 14.73 | 3.791 | 15.05 | 3.732 | 15.15 | 3.752 |
| 187.1 | 10.96 | 4.198 | 12.25 | 4.110 | 11.33 | 4.147 |
| 188.1 | 10.08 | 4.371 | | | | |
| 189.1 | 9.15 | 4.628 | | | | |

pressures to differ by 0.56° from the temperature scale used in this investigation. A shift in the Cardoso temperature scale of equal amount in this instance also brings the latter's observations into agreement with those here presented, thus confirming the opinion already stated that it is the temperature scales which are in disagreement rather than the pressure or volume measurements. In Table VI the second column gives the vapor volumes as given for the temperatures specified by Cardoso. The third column gives the Cardoso liquid volumes. Columns four and five contain the vapor and liquid volumes obtained in the present investigation at the same temperatures, and the sixth and seventh columns, the volumes of Cardoso corrected for the temperature difference 0.56. It is seen that substantial agreement is obtained, as was the case with the vapor pressures.

The specific volumes of the saturated vapor have always been exceedingly difficult to measure. The difficulty of obtaining true equilibrium, freedom from foreign gases, the complete drainage of the walls of the container, the relatively large fraction of the total mass necessarily present in the liquid phase, and surface adsorption are some of the difficulties encountered. Experimental experience has led almost to the conviction that the vapor specific volume cannot be accurately measured. In the case of ammonia it was found that the equation of state gave saturated vapor specific volumes which accorded with the actual observation within the unavoidable errors of experiment and the same statement is true as regards carbon dioxide.[9] At the low temperatures

[9] Keyes and Kenney, Jour. of Soc. Am. Ref. Engr., **3**, **1**, **1917**.

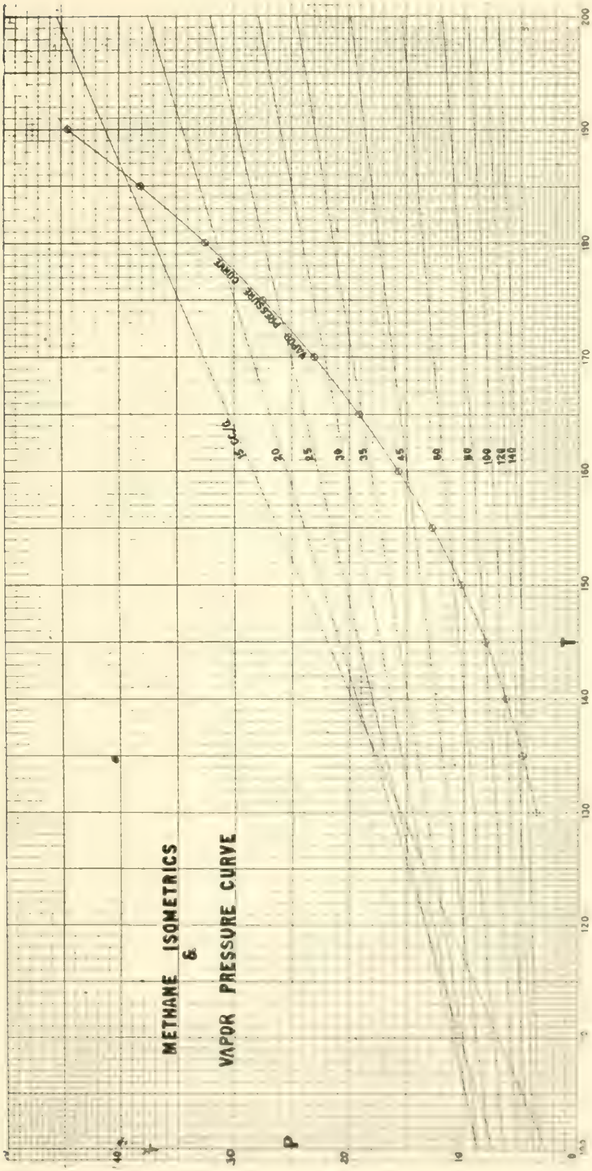
METHANE ISOMETRICS
&
VAPOR PRESSURE CURVE
VAPOR PRESSURE CURVE
15 cc/g
20
25
30
35
45
60
80
100
120
140
P
0
10
20
30
40
T
100
110
120
130
140
150
160
170
180
190
200

Fig. 5

encountered in the liquid range of methane some apprehension was felt concerning the reliability of using the methane equation of state to calculate the saturation specific volumes, but the enhanced difficulties of carrying out measurements at such low temperatures lead to the decision to calculate the volumes. In the case of nitrogen whose equation of state we possess, values are obtained which, when employed in the Clapeyron equation, give a value for the latent heat of vaporization agreeing well with the experimental number. It is, of course, evident that for the very large specific volumes (1,000 c.c./g.) the equation of state would be accurate. The doubt which may arise pertains to volumes from 200 c.c./g. to 30 c.c./g.

The plot of a number of the isometrics of methane is represented in Fig. 5, upon which has been placed the vapor pressures. The saturation specific volumes are the points of intersection of the isometrics with the pressure-temperature curve and this is, perhaps, the most convenient means of obtaining the vapor specific volumes. The final specific volumes for both phases are represented in the plot Fig. 6.

Table VII contains the saturation specific volumes and densities of methane vapor and liquid from 95° to the critical temperature for each five degrees. Volumes smaller than 35 c.c./g. were not

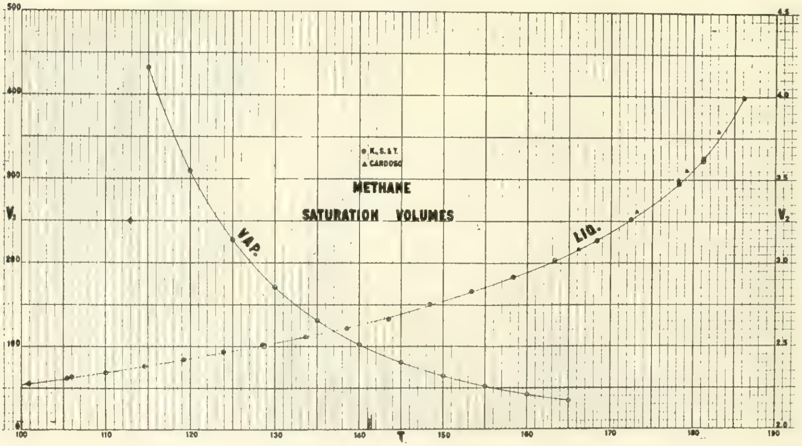

Fig. 6

computed, since association or polymerization may be supposed to exist in the smaller volumes and the equation of state applies only for the case where the completely unassociated methane molecules are present. The mean diameter equation can be used to obtain volumes smaller than 35 c.c./g.

TABLE VII
**M. I. T. Methane Data**

| *Temp. Deg. Abs.* | *Specific Volume Liquid c.c./gm.* | *Specific Volume sat'd vapor Keyes' eq. c.c./gm.* | *Density Liquid gm./c.c.* | *Density sat'd vapor Keyes' Eq. gm./c.c.* | *Density sat'd vapor from $d_m$ and Liquid Density. gm./c.c.* |
|---|---|---|---|---|---|
| 95 | | 2436.7 | | .0004104 | |
| 100 | 2.2691 | 1470.4 | .4417 | .0006801 | |
| 105 | 2.3069 | 936.9 | .4335 | .001067 | |
| 110 | 2.3458 | 624.7 | .4263 | .001601 | |
| 111.52 | 2.3580 | 556.9 | .4241 | .001796 | |
| 115 | 2.3865 | 432.7 | .4190 | .002311 | |
| 120 | 2.4291 | 309.4 | .4117 | .003232 | |
| 125 | 2.4735 | 227.4 | .4043 | .004398 | |
| 130 | 2.5208 | 171.0 | .3967 | .005850 | |
| 135 | 2.5719 | 131.0 | .3888 | .007632 | |
| 140 | 2.6288 | 102.1 | .3804 | .009794 | |
| 145 | 2.6937 | 80.63 | .3712 | .01240 | |
| 150 | 2.7683 | 64.43 | .3612 | .01552 | |
| 155 | 2.8533 | 51.96 | .3505 | .01925 | |
| 160 | 2.9491 | 42.22 | .3391 | .02369 | |
| 165 | 3.0496 | 34.49 | .3279 | .02899 | |
| 170 | 3.1881 | | .3137 | | .03667 |
| 175 | 3.3463 | | .2988 | | .04592 |
| 180 | 3.5565 | | .2812 | | .05598 |
| 185 | 3.8871 | | .2573 | | .07335 |
| 190 | | | | | |
| 191.03 Crit. | 6.2 | | .1613 | | .1613 |

The data of Cardoso relative to the saturation volumes were taken close to the critical temperature. However, in the range where the specific volumes were computed by means of the equation of state the following mean density equation was obtained:

$$Dm = 0.16134 + 0.00065723\ (Tc - T)$$

Cardoso gives the mean density equation based on his results.

$$Dm = 0.1623 + 0.0006064\ (Tc - T).$$

The agreement is very good and lends confidence to the computed values. Fig. 7 gives the densities obtained in the present investigation together with the uncorrected Cardoso values. The critical density, making the temperature correction 0.56, makes the critical density of Cardoso 0.1618, as compared with 0.1613 obtained in the present investigation.

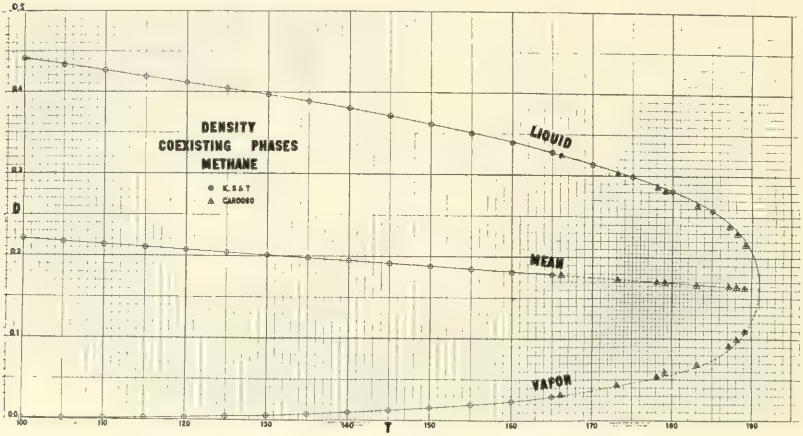

Fig. 7

6. **The Latent Heats of Evaporation.** A preliminary study has been made in the development of calorimetric methods that will permit the measurement of heats of evaporation and the specific heats of liquids at very low temperatures. At present, however, no experimental values are available for methane, but by means of the vapor pressure equation and the specific volumes of the coexisting phases, latent heats may be calculated by means of the Clapeyron equation.

The equation of the vapor pressure, (3), upon differentiation gives for $\frac{dp}{dt}$,

$$\frac{dp}{dT}=p\left[\frac{1371.298}{T^2}-0.093065+7.76685\times 10^{-4}T-1.73878\times 10^{-6}T^2\right]. \tag{4}$$

In Table VIII will be found in the first column the absolute temperature and in the succeeding columns the value of $\frac{dp}{dT}$,

## TABLE VIII

### Latent Heat of Evaporation

| $T$ | $\frac{dp}{dT}$ atms. | $V_1 \frac{c.c.}{g.}$ | $V_2 \frac{c.c.}{g.}$ | $\lambda \frac{cal.}{g.}$ | calc. |
|---|---|---|---|---|---|
| 100 | 0.03593 | 1470.4 | 2.2691 | 127.75 | 127.59 |
| 105 | 0.05290 | 936.9 | 2.3068 | 125.71 | 125.71 |
| 110 | 0.07461 | 624.7 | 2.3458 | 123.69 | 123.76 |
| 111.52 | 0.08214 | 556.8 | 2.3580 | 122.99 | Normal Boiling Pt. |
| 115 | 0.10152 | 432.7 | 2.3868 | 121.65 | 121.74 |
| 120 | 0.13403 | 309.4 | 2.4291 | 119.58 | 119.64 |
| 125 | 0.17249 | 227.4 | 2.4735 | 117.44 | 117.44 |
| 130 | 0.21723 | 171.0 | 2.5208 | 115.19 | 115.14 |
| 135 | 0.26856 | 131.0 | 2.5719 | 112.79 | 112.71 |
| 140 | 0.32677 | 102.7 | 2.6288 | 110.20 | 110.14 |
| 145 | 0.39214 | 80.6 | 2.6937 | 107.32 | 107.39 |
| 150 | 0.46493 | 64.4 | 2.7683 | 104.14 | 104.44 |
| 155 | 0.54535 | 51.96 | 2.8533 | 100.52 | 101.23 |
| 160 | 0.63363 | 42.22 | 2.9491 | 96.42 | 97.70 |
| 165 | 0.72975 | 34.49 | 3.0496 | 91.68 | 93.74 |

$V_1$, $V_2$ and the latent heat. On the basis of these latent heat values the following equation was composed relating the quantity to the temperature:

$$\log_{10}\lambda = 1.65214 + 2.0076 \times 10^{-4}(Tc - T) + 0.22225 \log_{10}(Tc - T). \quad (5)$$

There are no published data for the latent heat of evaporation of methane with the exception of an approximate value recently obtained due to Satterly and Patterson[10] who give 138 cal/g. ± 5%. This value refers to the temperature of the normal boiling point 111.52° at which temperature 123 cal/g is obtained in the present investigation. The experimental value is about ten per cent greater. The value of the mean specific heat of copper is involved in the measurement and an error in the true boiling point of methane enters in computing the latent heat from the experimental data. The methane evolved by the copper block dropped into the liquid was measured by collecting over water In a later paper experimental values obtained in this laboratory will be presented.

If the liquid phase consisted of completely polymerized double molecules or, in fact, was composed of molecules whose molecular species was constant with respect to temperature changes the internal heat of evaporation would be simply related to the specific volumes of the coexisting phases. Consider the thermodynamic equation: ,

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[10] Satterly and Patterson, Roy. Soc. Can. Trans. **13**, 123, 1919.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p. \tag{6}$$

Integration of this equation at constant temperature yields,

$$U_2 - U_1 = \int_{v_1}^{v_2}\left( T\left(\frac{\partial p}{\partial T}\right)_v - p \right)dv \tag{7}$$

and for an invariable species composing the liquid phase of specific volume, $v_2$, passing to a specific volume $v_1$ of the vapor phase the energy is represented by the work against the attractive forces of the molecules. Evaluating $\left(\frac{\partial p}{\partial T}\right)_v$ by means of the equation of state will give, then, a definite value for the right-hand member of Equation (7).

$$\int_{v_1}^{v_2}\left(T\frac{\partial p}{\partial T} - p\right)dv = \int_{v_1}^{v_2}\left(\frac{RT}{v-\delta} - p\right)dv = \int_{v_1}^{v_2}\frac{A}{(v-l)^2}\,dv,$$

or

$$\Delta U = U_1 - U_2 = A\left(\frac{1}{v_2 - l} - \frac{1}{v_1 - l}\right). \tag{8}$$

Now $\Delta U$ and the specific volumes of the coexisting phases may be plotted with $\frac{1}{\Delta U}$ and $v_2$ as coördinates giving a line which may be used as an approximation plot to roughly evaluate $l$ and $A$ and the data replotted, using as coördinates $\frac{1}{\Delta U + \frac{A}{v_1}}$ and $v_2$. The fact that a straight line is obtained may mean that the molecular state of the liquid is the same as that of the vapor in contact therewith, or it may mean that the molecular state of the liquid, for example, was that of substantially complete polymerization to double molecules or those of higher order; the vapor in contact consisting of substantially all single molecules. The value of $A$ in the latter case would be a certain mean value, then, between the value of $A$ for double molecules and single molecules. If the liquid, however, was composed of molecules of the same type as the vapor, the value of $A$ should be numerically equal to

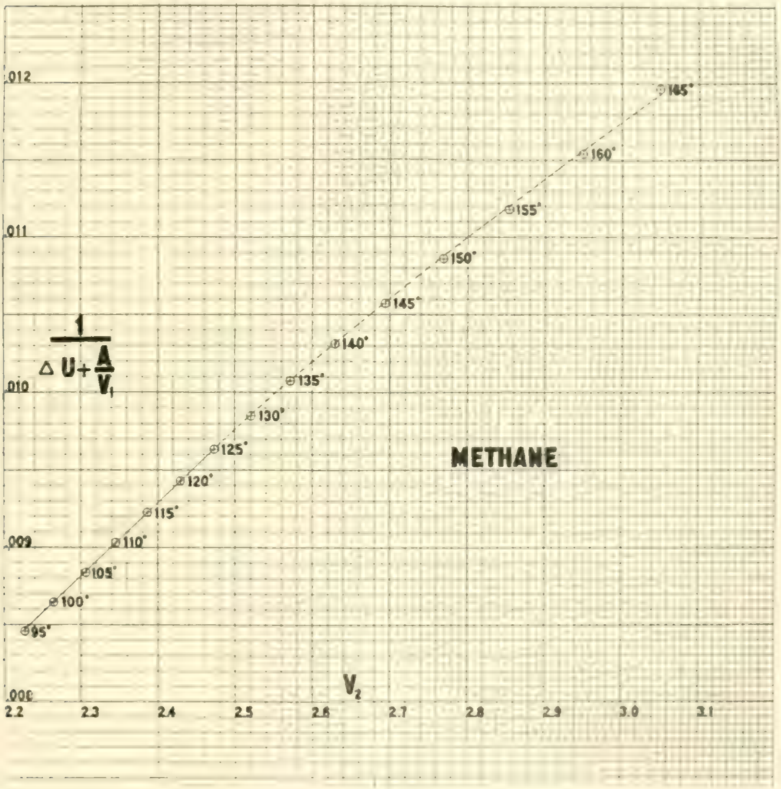

Fig. 8

$A$ obtained for the equation of state of methane. Moreover, if the data do not lie on a straight line in terms of the coordinates given, evidence is afforded that the relative molecular state in the coexisting phases is changing at higher temperatures. As a matter of fact the data of methane in the lower temperature range do lie on a straight line, but deviate as higher temperatures are approached. Also the numerical value of $A$ is not that found for the equation of state of methane composed of single molecules. Fig. 8 exhibits the methane data.

The further elaboration of the connection between the internal heat of evaporation and the equation of state has been waiting for some years for the completion of several investigations in progress in this laboratory. Very shortly, for example, there will appear the results in connection with liquid ether at low temperatures, which illustrate the linear relation between $\dfrac{1}{\Delta U+\dfrac{A}{v_1}}$ and $v_2$, and further papers, it is hoped, will follow promptly.

7. **The Specific Heats of the Coexisting Phases.** The experimental data for the vapor phase have been published by Regnault,[11] Lussana[12] and Heuse.[13] The latter data supersede the older work and measurements were made at the temperatures 15.0, 5.0, −30.0, −55.0, −81.0. The one atmosphere constant pressure values were computed to constant volume specific heats by means of the equation of state and from a plot values chosen at the absolute temperatures 150, 200, 250, 300 for the purpose of correlation as a function of the temperature. The equation obtained is,

$$C_v=0.3050+1.12\times10^{-3}T-6.45\times10^{-6}T^2+13.04\times10^{-9}T^3. \quad (9)$$

To obtain the constant pressure specific heat use may be made of the equation

$$C_p=C_v+T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p \quad (10)$$

which becomes using the equation of state for methane:

$$C_p=C_v+\frac{R/m}{1-\dfrac{\alpha\delta}{v^2}-\dfrac{2A}{RT}\,\dfrac{(v-\delta)^2}{(v+l)^3}}. \quad (11)$$

This equation is not valid in the critical region but will give accurate values along the saturation line to at least 35 c.c. per gram. For low pressures it suffices to replace (11) by the approximate equation:

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[11] Regnault. Mem. de l'Acad. **26,** 1, 1862.

[12] Lussana. Nouv. Cim. **36,** 5, 70, 130, 1894.

[13] Heuse. Ann. d. Phy. **59,** 94, 1919.

$$C_p = C_{p_0} + \frac{2A}{R} \cdot \frac{1}{T^2} p \tag{12}$$

where $C_{p_0}$ is the specific heat at very low pressures, being equal to $C_v + R/m$; $m$ representing the molecular weight in grams and $R$ the gas constant per mol in calories. The numerical equation corresponding to (12) is,

$$\begin{aligned} C_p &= 0.4288 + 1.12 \times 10^{-3} T \\ &- 6.45 \times 10^{-6} T^2 + 13.04 \times 10^{-9} T^3 + \frac{93}{T^2} p^{\text{atm.}} \end{aligned} \tag{13}$$

In Table IX will be found the comparison of the vapor specific heats computed by Equation (9) and the experimental values due to Heuse.

TABLE IX

The Gas Phase Specific Heat

| | 15.0 | 5.0 | −30.0 | −55.0 | −81.0 |
|---|---|---|---|---|---|
| $C_v$ Heuse | 0.4051 | 0.4000 | 0.3826 | 0.3782 | 0.3777 |
| $C_v$ Calculated | 0.4041 | 0.3982 | 0.3834 | 0.3778 | 0.3746 |

Regnault gives 0.593 cal. as the value of $C_p$ between 18 and 208 at one atmosphere. Equation (13), however, leads to 0.675 cal. Lussana gives 0.591 cal. between 11 and 95 at one atmosphere, whereas the equation gives 0.564 cal. Lussana gives the specific heat between 11 and 95 as a function of the pressure, as follows:

$$C_p = 0.5915 + 0.03463(p - 1)$$

whereas Equation (13) leads to

$$C_p = 0.5643 + 0.00089(p - 1).$$

The pressure coefficient of Lussana is nearly forty times as large as that given through the equation of state. In the case of air Lussana's pressure coefficient is also much greater than that given by the equation of state for air[14] Holborn and Jacobs,[15] however, recently measured the specific heat of air to 200 atms. and their mean pressure coefficient agrees almost exactly with that given through the equation of state. Carbon dioxide and ammonia furnished further examples and there can be little doubt but that Lussana's pressure coefficients are all too large.

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[14] Keyes, Jour. Amer. Chem. Soc. **43,** 1452, 1921.

[15] Holborn and Jacobs, Z. Ver. deut. Ing. **58,** 1429, 1914.

Facilities for measuring the specific heat of the liquid phase of substances have been under development for some years and shortly values will be available. In the meantime use may be made of the available data to calculate the liquid phase specific heat.

Consider the thermodynamic equation

$$C_{s_1}-C_{s_2}=T\frac{d\frac{\lambda}{T}}{dT} \tag{14}$$

where $C_{s_1}$ and $C_{s_2}$ denote the specific heat of the saturated gas and liquid phases respectively, while λ as before represents the latent heat of evaporation. The equation for $C_{s_1}$ is,

$$C_{s_1}=C_{p_1}-T\left(\frac{\partial v}{\partial T}\right)_p\frac{dp}{dT}$$

and $C_{p_1}=C_{v_1}+T\left(\frac{\partial p}{\partial T}\right)\cdot\left(\frac{\partial v}{\partial T}\right)$. By means of the equation of state the differential coefficients can be evaluated, while $C_v$ is given by the equation (9). The equation for $T\frac{d\frac{\lambda}{T}}{dT}$ can be formed from Equation (5) leading to

$$T\frac{d\frac{\lambda}{T}}{dT}=-\lambda\left[0.0004623+\frac{0.22225}{T_c-T}+\frac{1}{T}\right].$$

At 110° $C_{s_1}$ is $-0.689\frac{\text{cal.}}{\text{g.}}$ and $T\frac{d\frac{\lambda}{T}}{dT}$ equal to $-1.522$, giving $C_{s_2}$, the specific heat of the liquid, $0.833\frac{\text{cal.}}{\text{g.}}$. At 150° $C_{s_1}$ is $-0.489\frac{\text{cal.}}{\text{g.}}$ and $T\frac{d\frac{\lambda}{T}}{dT}$ equal to $-1.307$ giving $0.818\frac{\text{cal.}}{\text{g.}}$ for the liquid specific heat. The latter number would be expected to be larger than the former, but the specific heat value at 110° involves a long extrapolation by means of the gas phase constant volume specific heat Equation, (9). All that may be stated at present is that in the region of the boiling point the specific heat of the liquid is about $0.82\frac{\text{cal.}}{\text{g.}}$

## SUMMARY

1. The vapor pressure of methane has been measured over substantially the entire liquid phase region and correlated as a function of the temperature as follows:

$$\log_{10}p^{\text{atm.}} = -\frac{595.546}{T} + 8.09938 - 4.04175\times10^{-2}T + 1.68655\times10^{-4}T^2 - 2.51715\times10^{-7}T^3.$$

2. The liquid phase specific volumes have been measured from about 100° abs. to nearly the critical temperature, 191.03 abs. The saturation specific volumes of the vapor phase were computed by means of the equation of state of methane, using the values of the pressure computed for definite temperatures from the vapor pressure equation.

3. The critical temperature is found to be 191.03° abs. on the scale of the quartz constant volume hydrogen thermometer. The critical pressure amounts to 45.8 atms., while the critical volume computed from the mean diameter equation is 6.2 c.c./g.

4. The heat of evaporation was computed by the Clapeyron equation, using the derivative $\frac{dp}{dT}$ obtained by differentiation of the vapor pressure equation and the specific volumes of the coexisting phases. The following equation reproduces the values from 100° abs. to 150° abs. where $\lambda$ represents the heat of evaporation:

$$\log_{10}\lambda = 1.65214 + 2.0076\times10^{-4}(T_c - T) + 0.22225\log_{10}(T_c - T).$$

5. The specific heat of the gas phases may be represented by the following equation based on the experimental values of Heuse:

$$C_v = 0.3050 + 1.12 \times 10^{-3} T - 6.45 \times 10^{-6} T^2 + 13.04 \times 10^{-9} T^3.$$

6. The specific heat of the saturated liquid was computed by means of the thermodynamic equation

$$C_{s_2} = C_{s_1} - T \frac{d \frac{\lambda}{T}}{d T}$$

and found to be $0.82 \frac{\text{cal.}}{\text{g.}}$ in the neighborhood of the normal boiling point.

(Contribution from the Rogers Laboratory of Physics, Massachusetts Institute of Technology.)

# THE ESTABLISHING OF THE ABSOLUTE TEMPERATURE SCALE BELOW THE MELTING POINT OF ICE

By Frederick G. Keyes, Bailey Townshend and Louis H. Young

## CONTENTS

Part I

I. Introduction.
II. Definition of Temperature by the Constant Volume Gas Thermometer· Calculation of Temperature from the Observed Measurements.
III. The Relation between the Constant Volume Gas Scale and the Kelvin Thermodynamic Scale.
    (*a*) The Equation of State for Gases. Evidence that Pressure is a Linear Function of the Temperature at Constant Volume.
    (*b*) The Normal Sulfur Boiling Point.
    (*c*) Discussion of the Usual Corrections to the Constant Volume Thermometer.
    (*d*) Analysis of the Isothermals and Isometrics of Hydrogen. The Equation of State for Hydrogen. Joule-Thomson Coefficients and Inversion Temperatures of Hydrogen.
IV. Description of the Apparatus.
V. Sources of Error.
VI. Description of the Experiments.
    (*a*) Indirect Determination of the Dead Space Volume.
    (*b*) Coefficient of Pressure Increase of Nitrogen.
    (*c*) The Diffusion of Helium and Hydrogen Through Quartz.
    (*d*) Measurements with the Nitrogen Thermometer. Thermocouple Calibration. Platinum Resistance Thermometer Comparison. Boiling Points of Carbon Dioxide and Oxygen (preliminary).
    (*e*) Measurements with the Hydrogen Thermometer. Platinum Resistance Thermometer Comparison. Comparison of Nitrogen and Hydrogen Thermometers. Boiling Point of Oxygen. Boiling Point of Carbon Dioxide.

Part II

Freezing Points of Certain Organic Liquids and of Mercury and Ammonia.
    The Method.
    The Results.
Summary.

## I. Introduction

The field of experimental inquiry at low temperatures relative to the properties of matter is one which has benefited largely from the researches conducted at Professor Onnes' laboratory in Leiden. Here there have been developed ingenious methods for attacking the many varied problems among which the most fundamental is undoubtedly the devising of convenient and accurate temperature-measuring instruments, and the relating of their indications to the absolute temperature scale. Systematic investigations of notable importance in the measurement of low temperatures have also been carried out at the Reichsanstalt. The status of the general problem has, however, not reached that stage where the calibration of temperature indicators of the secondary class, such as the electrical resistance, pentane, or thermoelement thermometers, can be safely relied upon without the use of the gas thermometer. The fixed points, for example, worthy of most confidence are the normal boiling points of oxygen and carbon dioxide; the former of which lies at about $-183°$ and the latter at about $-78.5°$. Evidently more fixed points are needed, and, moreover, the investigations of Henning have shown that the platinum resistance thermometer departs in its indications widely from the Callendar formula which is satisfactory above the ice point. Cardoso in the case of the pentane thermometer has also pointed out special difficulties attending the use of this thermometer, so that confidence in the low temperature investigations being carried out in this Institute could only be realized by an independent study of the low-temperature scale.

The many careful researches on gas thermometry and general methods of temperature measurement have dealt in the main, of course, with ordinary and high temperatures, while the region below the ice point has not as yet received as much development as is necessary. Apart, moreover, from the immediate need of thermometric standardization below 0°C. collateral problems have deterred progress in this direction. Chief of these is the relative difficulty of producing low temperatures and the extreme difficulty of maintaining these temperatures constant over considerable periods of time. In gas thermometry there is also the uncertainty with regard to the expansion of the container of the thermometric substance, and the effect of aggravated adsorption of the gas on the walls of the thermometer bulb. Indeed, it will be shown that this latter effect may be very appreciable and leads to serious error in the case of gases readily adsorbed. For some time this laboratory has had developed an improved type of cryostat wherein constancy of temperature of 0.01°C. is easily attainable, and certain other instrumental refinements, making it worth while to study the subject independently, from a slightly different standpoint, and with a view to increasing the accuracy of low temperature measurements.

The investigation set forth in the following pages has had for its primary objects: first, a study of the gas thermometer of constant volume between 0°C. and the boiling point of oxygen (−183°) and, second, the determination of certain fixed points within this range serving the same purpose as those now available for calibration of secondary instruments at temperatures above the ice point. Incident hereto was, of course, a comparison of the platinum resistance thermometer and copper-constantan thermocouple used in other low temperature investigations with the hydrogen constant volume thermometric scale.

## II. Calculation of Temperature from Observed Measurements with the Constant Volume Gas Thermometer.

Centigrade temperature is defined by the equation:

$$t=\frac{p-p_\circ}{\overset{t}{\underset{\circ}{\epsilon}}{}_v p_\circ} \tag{1}$$

where $p$ and $p_\circ$ are the pressures exerted by the gas at $t°$ and $0°$ respectively, and $\overset{t}{\underset{\circ}{\epsilon}}{}_v$ is the mean coefficient of pressure increase at constant volume between $0°$ and $t°$. The two fixed points defined by the freezing point and normal boiling point of water are, of course, the usual temperature interval used.

Since the volume of the container is not absolutely constant, owing to temperature dilation and pressure dilation changes, it is necessary to modify (1) to

$$t=\frac{p\frac{v}{v_0}-p_0}{\overset{t}{\underset{0}{\epsilon}}{}_v\, p_0} \tag{2}$$

where $v$ and $v_0$ are the true volumes at $t°$ and $0°$.

The system containing the gas comprises the bulb of the thermometer and a certain length of capillary connecting the bulb to the manometer. Let the volume of this latter part be designated as "dead space" and the following symbols adopted:

$V_0$ = volume of bulb at 0°.
$V$ = volume of bulb at $t°$.
$v_s$ = volume of dead space at room temperature.[1]
$\beta$ = coefficient of cubical expansion of bulb material.
$\delta$ = coefficient of expansion of the bulb with internal pressure (c.c. per mm.)

Then (2) becomes

$$t=\frac{1}{\overset{t}{\underset{0}{\epsilon}}{}_v\, p_0}\left[p\frac{V_0+v_s}{V_0+v_s}-p_0\right]$$

or

$$t=\frac{1}{\overset{t}{\underset{0}{\epsilon}}{}_v\, p_0}\left[p\left\{1+\frac{\beta t V_0+\delta(p-p_0)}{V_0+v_s}\right\}-p_0\right] \quad . \; . \; . \tag{3}$$

### *Dead Space Correction*

In the above formula the pressures are those which the gas would exert if the entire volume were at $t°$ and 0° respectively. In practice, the bulb and a certain portion of the capillary are at the temperature of the bath, while the remainder of the dead space may be divided into parts at $t°_1$, $t°_2$, etc. The manner of computing $p$ from the corrected observed pressure, $p^{\mathrm{I}}$, is as follows: Let

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[1] The volume of the dead space is relatively small and since the temperature of the greater part of it is always within a few degrees of the same value it is not necessary to consider its volume change due to temperature and pressure.

$V$ = volume of the bulb at the temperature of the bath, $t$.
$v_1$, $v_2$, etc. = volumes of dead space at corresponding temperature, $t_1$, $t_2$, etc.
$\epsilon$ = approximate coefficient of expansion of a gas, 0.00366.

Then, making use of the fact that the total mass of gas in the apparatus is constant:

$$p\frac{(V+v_1+v_2+\ \dots)}{1+\epsilon t}=\frac{p^{\mathrm{I}}V}{1+\epsilon t}+\frac{p^{\mathrm{I}}v_1}{1+\epsilon t_1}+\frac{p^{\mathrm{I}}v_2}{1+\epsilon t_2}+\ \dots$$

from which it follows that:

$$p-p^{\mathrm{I}}=p^{\mathrm{I}}\left\{\frac{v_1(1+\epsilon t_2)(t-t_1)\epsilon+v_2(1+\epsilon t_2)(t_1-t_2)\epsilon}{(V+v_1+v_2)(1+\epsilon t_1)(1+\epsilon t_2)}\right\}\ \dots \tag{4}$$

where the dead space is considered in this example as consisting of two portions, $v_1$ and $v_2$.

### *Correction of the Observed Pressure*

The pressures are here expressed in millimeters of mercury. To obtain $p^{\mathrm{I}}$ the actually observed height must be corrected to millimeters of Hg at 0°, sea level, and 45° latitude and also for difference in level of the bulb and contact point of the manometer.[2] The former involves a knowledge of calibration errors and coefficient of expansion of the cathetometer scale. Let

$\gamma$ = coefficient of linear expansion of cathetometer scale.
$\sigma$ = scale error per millimeter as compared with standard scale at 20°.
$p^{\mathrm{IV}}$ = actually observed pressure.
$p^{\mathrm{III}}$ = pressure corrected for cathetometer scale errors.
$t_r$ = room temperature.

then

$$p^{\mathrm{III}}=p^{\mathrm{IV}}\{1+\sigma+\gamma(t_r-20)\} \tag{5a}$$

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[2] A correction for capillary depression may be eliminated by using manometer tubes of sufficiently large and uniform diameter.

Further let

$t_m$ = temperature of mercury column of manometer.

$\alpha$ = mean coefficient of expansion of mercury 0° to $t_m^o$.

$g$ = acceleration of gravity at place of observation.

$G$ = standard acceleration of gravity.

$p^{\text{II}}$ = pressure corrected for scale errors and reduced to standard conditions.

Then

$$p^{\text{II}} = p^{\text{III}}\left(\frac{g}{G}\right)\left(1-\alpha t_m\right) \tag{5b}$$

The level correction is significant where the difference in level is several hundred millimeters. Let

$l$ = height of bulb above contact point of manometer.

$\rho_g$ = density of the gas at temperature of column 1.

$\rho_m$ = density of mercury at 0°.

$p$ = pressure corrected for scale errors, reduced to standard conditions, and corrected for difference in gas level.

Then

$$p^{\text{I}} = p^{\text{II}} - \frac{\rho_g l}{\rho_m} \tag{5c}$$

Combining into one formula the various corrections applicable to the observed height, $p,^{\text{IV}}$ and excepting the dead space correction, there results:

$$p^{\text{I}} = p^{\text{IV}}\left\{1+\sigma+\gamma(t_r-20)\right\}\left(\frac{g}{G}\right)\left(1-\alpha t_m\right)-\frac{\rho_g l}{\rho_m} \tag{6}$$

Formulæ (3), (4) and (6) thus serve to calculate the centigrade temperatures from the actually observed difference in height of the mercury columns of the manometer, it being assumed that the space above the variable column is exhausted.

A quantitative discussion of sources of error will be given in connection with the description of the experimental procedure. It will be, however, instructive at this point to present a sample calculation illustrating the magnitudes of the various corrections.

The following is a measurement of the temperature of liquid oxygen (above its normal boiling point) by means of the hydrogen thermometer.

| $p^{\mathrm{IV}}$ mm. | $t_m$ | $t_r$ | *Time* (3/30/22) |
|---|---|---|---|
| 255.430 | 23.16 | 25.0 | 10.50 |
| 255.423 | 23.17 | 25.0 | .52 |
| 233.430 | 23.18 | 25.0 | .57 |
| 255.435 | 23.20 | 25.0 | .59 |

For the correction for scale and reduction of mercury column to standard conditions (5a), (5b),

$$p^{\mathrm{II}} = 255.430\,[1+20\times10^{-6}+11\times10^{-6}(25-10)][1-0.000255]\,[1-1.809\times10^{-4}(23.18)] = 254.313 \text{ mm.}$$

For the correction for difference in level of the bulb and contact point of manometer (5c),

$$p^{\mathrm{I}} = 254.313 - \frac{0.00038\times300}{13.5} = 254.305 \text{ mm.}$$

Correction for dead space:

$$p - p^{\mathrm{I}} = 254.3\left[\frac{.0133(1+23.2\epsilon)(-103\epsilon)+.764(1-79.9\epsilon)(-206\epsilon)}{92.7(1+23.2\epsilon)(1-79.9\epsilon)}\right] = -1.49 \text{ mm.}$$

Whereupon

$$p = 252.82 \text{ mm.}$$

Calculation of the temperature: $p_0 = 763.17$ mm.

From (3) $\overset{100}{\underset{0}{\epsilon}}_v = 0.0036623$

$$t = \frac{1}{p_0\overset{t}{\underset{0}{\epsilon}}_v}[252.82(1-0.000013)-763.17] = -182.60°\mathrm{C}$$

## III. The Relation Between the Constant Volume Gas Scale and the Kelvin Thermodynamic Scale

The international practical scale of temperature is that of the hydrogen constant volume thermometer with initial pressure (0°C.) of one thousand millimeters of mercury.[3] At the time of this definition, hydrogen was the most nearly "perfect" gas known and the deviations of its scale from the absolute thermodynamic scale were supposedly no greater than the experimental error of gas thermometry. The scientific definition of temperature is contained in the second law of thermodynamics and it becomes a matter of fundamental importance to interpret the temperature indications of the constant volume gas thermometer with the rational thermodynamic scale or Kelvin[4] scale.

Consider the thermodynamic relation expressing the dependence of the internal energy, $U$, of a gas upon its volume at constant temperature:

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p$$

$$= T^2\left\{\frac{\partial (p/T)}{\partial T}\right\}_v \tag{7}$$

If $(\delta U/\delta v)_T = 0$ as in the case of the perfect gas, we obtain from (7):

$$\frac{p}{T} - \frac{p_\circ}{T_\circ} = 0 \quad \text{at constant volume.}$$

$$T_\circ(p - p_\circ) - p_\circ t = 0$$

or

$$t = \frac{p - p_\circ}{\epsilon p_\circ} \tag{8}$$

where $\epsilon = 1/T_\circ$ by definition. (8) gives our fundamental definition of centigrade temperature in terms of the constant volume "perfect gas" thermometer.

For an actual gas $(\delta U/\delta_v)_T \neq 0$ and the gas scale temperature is therefore defined by (1), *viz.:*

$$t = \frac{p - p_\circ}{\overset{t}{\underset{\circ}{\epsilon}}_v\, p_\circ}$$

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[3] Comité international des Poids et Mesures, Oct. 15, 1887.

[4] Lord Kelvin, Math. and Phys. Papers, Vol. **1**, p. 100, 1848.

Designate the quantity $(\delta U/\delta v)_T$ by $\lambda$, where $\lambda$ may be a function of the absolute temperature, designated by $T$. Then in general we have for the constant volume thermometer:

$$\frac{p}{T}-\frac{p_0}{T_0}=\int_{T_0}^{T}\frac{\lambda}{T^2}dT \qquad (9)$$

Putting, for brevity, $\displaystyle\int_{T_0}^{T}\frac{\lambda}{T^2}dT=I=\frac{T_0(p-p_0)-p_0t}{T\;T_0}$

whence, since $\displaystyle\frac{p-p_0}{p_0t}=\overset{t}{\underset{0}{\epsilon_v}}$, $\quad\displaystyle\overset{t}{\underset{0}{\epsilon_v}}=\epsilon+\frac{T\;I}{p_0t}$ (10)

where $\epsilon$ is the expansion coefficient of a perfect gas, or $1/T_0$. Equation (10) would serve to evaluate $\overset{t}{\underset{0}{\epsilon_v}}$ for any gas, provided there were means of determining $\lambda$, and hence $I$. $\lambda$ has not been successfully measured experimentally.

It is to be noted that the temperature given by (1) is the true centigrade temperature by definition of $\overset{t}{\underset{0}{\epsilon_v}}$. In using this equation it has been customary to put for $\overset{t}{\underset{0}{\epsilon_v}}$ the measured mean pressure coefficient between 0°C. and 100°C., namely, $\overset{100}{\underset{0}{\epsilon_v}}$. In this case there results.

$$t_g=\frac{p-p_0}{\overset{100}{\underset{0}{\epsilon_v}}\,p_0} \qquad (11)$$

and

$$t_g-t=t.\;\frac{\overset{t}{\underset{0}{\epsilon_v}}-\overset{100}{\underset{0}{\epsilon_v}}}{\overset{100}{\underset{0}{\epsilon_v}}}$$

Obviously, if the pressure is a linear function of the temperature at constant volume, $t_g-t=0$, and the temperature given by (11) needs no correction.

## *A. The Equation of State for Gases*

Much evidence has recently come to hand, that in a gaseous system composed of invariable species of molecule* the pressure at constant volume actually varies linearly with the temperature. Ramsay and Young[5] reached this conclusion from a study of the ether and carbon dioxide isometrics. The equation of Van der Waals, moreover, is of this form, and the equation of state deduced by Keyes[6,7,8]:

$$p=\frac{RT}{v-\delta}-\frac{A}{(v-l)^2} \tag{12}$$

where $\delta=\beta e^{-a/v}$ for polyatomic gases and $\delta=\beta$ for monatomic gases requires a linear increase of pressure with temperature. The satisfactory agreement of this equation with the experimental data on nitrogen, air argon, hydrogen, helium, carbon dioxide, ammonia, steam, ether, methane, and isopentane make it seem highly probable that it represents the facts well within the experimental error. Once given an equation of state it becomes possible, of course, to calculate such quantities as $\overset{t}{\underset{o}{\epsilon}}_v$, $\overset{t}{\underset{o}{\epsilon}}_p$, the Joule-Thomson coefficient $\mu$, $\frac{\partial(p_v)}{\partial p}$, and also the absolute ice point temperature, $T_o$. The agreement of the results of such calculations with experiment furnishes additional and critical evidence of the validity of the form of the equation. With these results the conclusion is reached that the constant volume gas thermometer, operated within the range where the species of molecule is invariable, and where adsorption of the gas upon the walls of the container is not a factor, indicates the absolute thermodynamic temperature without correction.

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* *i.e.* dissociation or association must not take place within the contemplated range.

[5] Nature, **44,** pp. 276, 608, 1891 ; also Preston, Theory of Heat (3 ed.), p.460.

[6] Keyes, Proc. Nat. Acad. Sci. **3,** p. 323, 1917.

[7] Phillips, This Jour., **1,** p. 42, 1921.

[8] Keyes, Jour. Am. Soc. Refrig. Engrs., **1,** 9, 1914.
Keyes, Jour. Am. Chem. Soc., **41,** 589, 1919.
Keyes, Jour. Am. Chem. Soc., **42,** 54, 1920.
Keyes, Jour. Am. Soc. Refrig. Engrs. **7,** 371, 1921.
Keyes, Jour. Am. Chem. Soc., **43,** 1452, 1921.
Keyes, This Jour. **1,** 89, 1922.

This conclusion can, however, be subjected to direct experimental test; for if there is a thermodynamic correction it must be proportional to the initial pressure of the gas[9] and may be determined by measuring the same temperature at different initial pressures and extrapolating to zero initial pressure. Thus, if the measured temperatures plotted against the initial pressure give a straight line which is not horizontal, it may be concluded there is a thermodynamic correction. On the other hand, if it is found that a curved line results, the deviations must be laid in part at least to some source other than an intrinsic property of the gas, such as adsorption, or a change in the molecular species of the thermometric gas. Measurements of this sort, using nitrogen as the thermometric gas, for which the correction is supposed to be relatively large, were made. The comparison temperature was that of liquid air, and the readings were referred to the same actual temperature by means of a multiple thermocouple, sensitive to 0.01°C., immersed with the gas thermometer. The mean of several determinations at each initial pressure has been plotted against the initial pressure in Fig. 1. It will be seen that the mean of determinations at approximately 640 mm. agrees with those

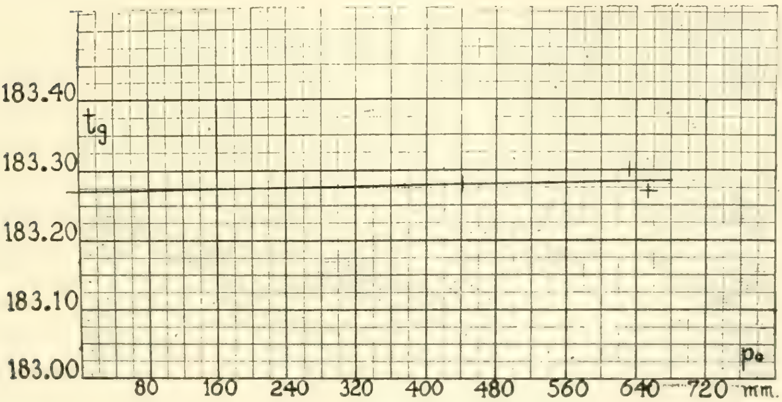

Fig. 1

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[9] F. Henning, Temperaturmessung (F. Vieweg u. Sohn, 1915), p. 67.

at 440 mm. within the experimental error. According to the corrections to the constant volume nitrogen scale calculated by D. Berthelot,[10] however, the measured temperatures at these two initial pressures should have differed by 0.12°. In point of fact they are seen to differ by less than 0.01°.

We shall find that the nitrogen thermometer, however, does differ in its indications from those of the hydrogen thermometer at liquid air temperatures by about as much as 0.6°C. This deviation is explainable by adsorption of the gas on the walls of its container, or polymerization of the nitrogen, as will be shown in discussing the direct comparison of the two thermometers.

### *B. The Normal Sulfur Boiling Point*

The errors that may be introduced by surface effects of the container are impressively illustrated in the discrepancies in the measurements of the pressure and volume coefficients of gases by various observers. For illustration, consider the careful and representative measurements of the boiling point of sulfur by Holborn and Henning[11] and by Eumorfopoulos[12]. The latter used a Callendar constant-pressure nitrogen thermometer with quartz bulbs. The nitrogen was prepared and the instrument loaded in such a way as to insure the purity of the gas. It was found, that after pumping out this loading and evacuating at 500°C, the coefficient of expansion of a new loading was appreciably lower than that of the first. Several repetitions of this process finally reduced the measured coefficient to a constant value. A similar effect was observed in other sets of experiments. In each case, the final value of the coefficient agrees excellently with that calculated by means of the nitrogen equation of state of Keyes (12). These results are shown in the following table. Between successive observations the bulb was heated to 500°C. and thoroughly exhausted. Eumorfopoulos chose the final values of the volume coefficient of each series in the calculation of the temperature of boiling sulfur.

[10] Berthelot, Trav. et Mem. Bur. Int. **13,** 1907.
[11] Holborn and Henning, Ann. d. Phys. **35,** p. 761, 1911.
[12] Eumorfopoulos, Proc. Roy. Soc. **90,** A, p. 189, 1914.

TABLE I

| | *Initial Pressure mm.* | $\epsilon_{p\,0}^{100} \times 10^7$ *Obs.* | $\epsilon_{p\,0}^{100} \times 10^7$ *Calc.* | *Obs.-Calc.* $\times 10^7$ |
|---|---|---|---|---|
| First Series | 760 | 36714 | 36695 | 19 |
| | 763 | 36702 | 36696 | 6 |
| | 784 | 36702 | 36698 | 4 |
| Second Series | 756 | 36728 | 36695 | 33 |
| | 756 | 36704 | 36695 | 9 |
| | 757 | 36701 | 36995 | 6 |
| | 757 | 36699 | 36995 | 4 |

The foregoing results clearly indicate the necessity of repeated loading and exhausting at high temperature, and the unreliability of measurements where this precaution has not been taken. The following table gives a comparison of the finally accepted coefficients at the various initial pressures used by Eumorfopoulos with those calculated from the equation of state:

TABLE II

| *Initial Pressure mm.* | *Obs.* $\times 10^7$ | *Calc.* $\times 10^7$ | *Obs. – Calc.* $\times 10^7$ |
|---|---|---|---|
| 792 | 36701 | 36699 | 2 |
| 784 | 36702 | 36698 | 4 |
| 757 | 36699 | 36695 | 4 |
| 415 | 36659 | 36657 | 2 |
| 395 | 36656 | 36655 | 1 |

By extrapolation of the experimental values to zero pressure, Eumorfopoulos found the coefficient of the perfect gas to be 0.0036613; giving the ice point on the thermodynamic scale as 273.13°C., which is in almost exact agreement with the value calculated by Keyes[13] several years ago from (12), and also obtained by Buckingham[14] from a study of the available Joule-Thomson data.

The normal sulfur boiling point was measured at these different initial pressures and the values extrapolated to zero pressure to obtain the N.B.P. on the thermodynamic scale. Eumorfopoulos found this to be 444.61°C. If we take the various actually observed boiling points and apply to each the thermodynamic correction for the constant pressure nitrogen scale calculated from the equation of state (12) we find the following values:

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[13] Keyes, Jour. Am. Chem. Soc., **42,** 54 (1920).

[14] Buckingham, Bull. Bur. Stand., **3,** 237 (1907).

TABLE III

| *Initial Pressure mm.* | *Temp. Obs.* | *Normal S.B.P. Corr.* |
|---|---|---|
| 792 | 444.13 | 444.53 |
| 784 | 444.14 | 444.53 |
| 757 | 444.13 | 444.51 |
| 415 | 444.36 | 444.57 |
| 395 | 444.39 | 444.59 |
| | | 444.55 mean. |

Consider the work of Holborn and Henning on this same fixed point. They employed platinum resistance thermometers which had been directly compared with the constant volume gas thermometers of helium, hydrogen and nitrogen. The value obtained from the comparison with helium and hydrogen was 444.51°C. and considered final, since the thermodynamic correction to these scales was assumed less than the experimental error. From the comparison with the nitrogen gas thermometer, however, they found the value 444.43 C. To this value they applied the Berthelot correction, thus bringing it up to 444.59°C. The application of the correction evidently does not diminish the discrepancy between the two values, but merely changes its sign. A study of their results brings out, nevertheless, certain inconsistencies in the measurements of the pressure coefficients of nitrogen. Thus, the mean of the nitrogen coefficients measured in a quartz container at 621 mm. was 0.0036684, whereas two series in Jena glass gave 0.0036704 (at 631 mm.), and 0.0036710 (at 621 mm.). For helium and hydrogen, the measured coefficients were 0.0036618 (at 612 mm.), and 0.0036625 (at 623 mm.) respectively. These coefficients seem too large — for helium and hydrogen only very slightly (1 part in 10,000), for nitrogen decidedly (1 part in 3060) — on comparison with the values computed from (12). If we assume the calculated values correct, the gas thermometer temperatures become 444.55°C. on the helium and hydrogen scales, and 444.57°C on the nitrogen scale. Using, therefore, the gas expansion coefficients calculated from the equation of state of Keyes, and making no correction to the constant volume thermometer while using the corrections for the constant pressure nitrogen scale as computed by Keyes, there results the following excellent agreement in the sulfur N.B.P.

**TABLE IV**
**Normal Sulfur Boiling Point**

| *Observer* | *Gas Thermometer*<br>*Gas* | <br>*Constant* | *t.* |
|---|---|---|---|
| Holborn and Henning, 1911 | He, $H_2$ | Volume | 444.55 |
| Holborn and Henning, 1911 | $N_2$ | Volume | 444.57 |
| Eumorfopoulos, 1914 | $N_2$ | Pressure | 444.55 |

*C. The Usual Corrections to the Constant Volume Thermometer*

The discussion of this subject would be incomplete without a critical review of the methods which have been used by Rose-Innes[15], Berthelot[16], Buckingham[17], and Callendar[18] in computing corrections for constant pressure and constant volume gas thermometers.*

Rose-Innes assumed that the Joule-Thomson data for hydrogen and nitrogen could be represented by

$$\mu C_p{}^{**} = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2}$$

From this an equation of state

$$pv = RT - p\left[a_0 + \frac{a_1}{2T} + \frac{a_2}{3T^2}\right]$$

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[15] Rose-Innes, Phil. Mag. (6), **2**, p. 130, 1901 and Phil. Mag. (6), *15*, p. 301, 1908.

[16] Berthelot, Mem. Trav. Bur. Int., **13**, 1907.

[17] Buckingham, Bull. Bur. Stan., **3**, 237, 1907.

[18] Callendar, Phil. Mag. (6), **5**, p. 48, 1903.

* For a resumé of the various methods see Henning, Temperaturmessung, p. 72.

** $\mu C_p$ is defined from the thermodynamic equation for the Joule-Thomson effect, namely,

$$\mu C_p = \frac{\partial T}{\partial p} C_p = T\left(\frac{\partial v}{\partial T}\right)_p - v$$

is derived subject to the condition that

$$\left\{\frac{\partial(pv)}{\partial p}\right\}_T = -\left[a_\circ + \frac{a_1}{2T} + \frac{a_2}{3T^2}\right]$$

It follows then that the correction to the constant volume scale is

$$[t_g]_v - t = \frac{a_2}{3v}\,\frac{(t-t_\circ)(t-t_1)}{tt_\circ t_1}$$

and the correction to the constant pressure scale is

$$[t_g]_p - t = \frac{(t-t_\circ)(t-t_1)}{tt_1}\left\{\frac{a_1}{2V_\circ} + \frac{a_2}{3V_\circ}\left(\frac{1}{t} + \frac{1}{t_\circ} + \frac{1}{t_1}\right)\right\}$$

where the subscripts 0 and 1 refer to the freezing and boiling points of water. The constants $a_0$, $a_1$, $a_2$ were evaluated from Joule-Thomson data and the compressibility data of Amagat and of Chappuis.

Berthelot, on the assumption that the isotherms $(pv, p)$ are straight lines within the region of gas thermometer pressure, found the following correction equations:

$$[t_g]_v - t = p_\circ\left[273(t-100)\left\{\frac{\partial(pv)}{\partial p}\right\}_\circ - 3.73t\left\{\frac{\partial(pv)}{\partial p}\right\}_{100} + (273+t)\left\{\frac{\partial(pv)}{\partial p}\right\}_t\right]$$

$$[t_g]_p - t = 2.73p_\circ\left[(t-100)\left\{\frac{\partial(pv)}{\partial p}\right\}_\circ - t\left\{\frac{\partial(pv)}{\partial p}\right\}_{100} + 100\left\{\frac{\partial(pv)}{\partial p}\right\}\right]$$

Values of $\frac{\partial(pv)}{\partial p}$ were taken from various sources, and the range extended by means of the law of corresponding states.

Buckingham extended the range of Joule-Thomson coefficients by means of the law of corresponding states, and then calculated the correction to the constant pressure thermometer from the relation.

$$t-[t_g]_p=[t_g]_p\frac{T_\circ-T'_\circ}{T_1}-T'\frac{p_\circ}{R}\int_{T'_\circ}^{T'}\frac{\mu' C_p dT'}{T'}$$

The corrections* to the constant volume scale were derived from a combination of the above with isothermal data, according to the relation

$$[t_g]_p-[t_g]_v=[t_g]_v\frac{\overset{100}{\underset{\circ}{\epsilon_v}}}{\overset{100}{\underset{\circ}{\epsilon_p}}}\left[\frac{\overset{100}{\underset{\circ}{\epsilon_v}}-\overset{100}{\underset{\circ}{\epsilon_p}}}{\overset{100}{\underset{\circ}{\epsilon_v}}}-p_\circ\left(\frac{\partial(pv)}{\partial p}\right)\right]$$

To obtain $\left\{\frac{\partial(pv)}{\partial p}\right\}_t$ Buckingham used the equation of Berthelot: on the other hand $\left\{\frac{\partial(pv)}{\partial p}\right\}_T=b-\frac{a}{RT^2}$

Callendar, on the other hand, based his calculations upon an equation of state of the Clausius-Nerthelot form

$$pv=RT+p\left(b-\frac{a}{RT^n}\right)$$

where $n$ was taken as a characteristic constant of the gas, 0.5 for monatomic, 1.5 for diatomic, and 2.3 for polyatomic gases.

The two outstanding features of the four investigations outlined above are: (1) the assumption of a $\left(\frac{\partial(pv)}{\partial p}\right)_T$ function at ordinary pressures in inverse powers of $T$, and (2) the assumption of the validity of the law of corresponding states in extending the range of values of $\left(\frac{\partial(pv)}{\partial p}\right)_T$ and $\mu$.

To determine the correctness of the first of these assumptions it is simply necessary to plot experimental values of $\left(\frac{\partial(pv)}{\partial p}\right)_T$ against $1/T$. This has been done[19] for hydrogen, nitrogen, and carbon dioxide from the results of Chappuis, Rayleigh, Leduc,

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[19] Keyes, J. Math. Phys. M. I. T., **1**, 89, 1922.

* The prime refers to quantities measured on the gas scale.

Leduc and Sacerdot, Schalkwijk, and Jaquerod and Scheurer. In each case a straight line is the most representative one that can be drawn. Thus the form of the function at the pressures used in gas thermometry is

$$\left\{\frac{\partial(pv)}{\partial p}\right\}_T=a+\frac{b}{T}$$

From this it follows

$$pv=\left(a+\frac{b}{T}\right)p+f(T)$$

and, since at very low pressures $pv=f(T)=RT$, we have

$$pv=RT+p\left(a+\frac{b}{T}\right)$$

In the second term $p$ may be replaced by $RT/v$, giving

$$pv=RT\left(1+\frac{a}{v}\right)+\frac{Rb}{v}$$

$$=\frac{RTv}{v-a}+\frac{Rb}{v}$$

so that

$$p=\frac{RT}{v-a}+\frac{Rb}{v^2}$$

an equation of the type of (12) at low pressures and showing the pressure to be a linear function of the temperature at constant volume.

Assumption (2), involving the use of the law of corresponding states, is questionable. It has been shown to be invalid on the basis of the experimental data. The equation of state of Keyes indicates that the law is in general only true for monatomic substances and then with certain modifications over the usual form of statement. In the latter case, the values of the critical constants to be taken are not those experimentally measured at the true critical point, but rather the values at the critical point the substance would have if it conformed to its equation of state, right up to the point of condensation. This, in general, is not the case, owing to association of the molecules as the specific volume approaches that of the liquid.

### *D. Analysis of the Isothermals and Isometrics of Hydrogen*

Finally, mention should be made of the investigation of Kamerlingh Onnes and Braak[20] in which corrections for the constant volume hydrogen thermometer were determined from direct observations of the isotherms of hydrogen. The isotherms were

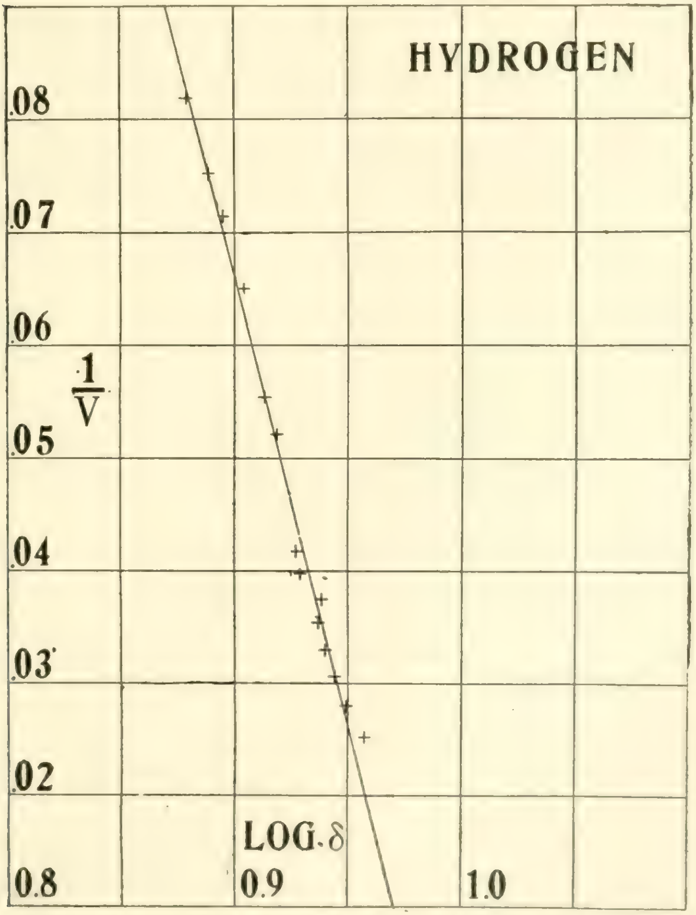

Fig. 2

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[20] Onnes and Braak, Leiden Comm. Nos. **97** (1906); 99a, 100a (1907).

here represented as a function of the inverse volume, namely,

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v^2{}_A} + \frac{D_A}{v^4{}_A} + \frac{E_A}{v^6{}_A} + \frac{F_A}{v^8{}_A} + \ldots$$

where the subscript $_A$ denotes values on the absolute scale. Since the actual measurements are referred to the hydrogen constant volume scale, the coefficients first calculated for this expression are an approximation. They can be used to determine provisional corrections to the temperature scale and then, with these, better values for the constants can be found. This method of successive approximations is applied until no change results from a repetition of the process.

In general the number of observations on any one isotherm were no greater than the number of " virial coefficients " chosen to represent it. Complete accordance between observed and calculated values can thus be obtained; but it must be remarked that the final equation embodies whatever errors there may have been in the measurements themselves. It may not happen, for example, that such an equation would be the best representative line that could be drawn through the data.

The constants for hydrogen in the Keyes equation of state were evaluated from data of Amagat and of Onnes and Braak. The Amagat data covered the range from 0° to 200° and from them the $\delta$ function could be determined. The relative magnitude of the $\frac{A}{(v\text{-}l)^2}$ term is so small here, however, that the constants $A$ and $l$ could not be found at all accurately. For this purpose, recourse was had to measurements at low temperatures, using the value of $\delta$ previously determined. In Fig. 2, log $\delta$ is plotted against $1/v$ for the Amagat data. The points give a straight line, the equation of which is $\log \delta = \log \beta - \alpha/v$. With the $\delta$ function determined in this way, we may calculate $\phi$, $\left(\frac{A}{(v-l)^2}\right)$, from the data of the observers listed in Fig. 3 and plot the volume against $\frac{1}{\sqrt{\phi}}$ as is here done. The best representative line is again straight, and from it the constants $A$ and $l$ are determinable. The inconsistency of the various measurements at low temperatures is apparent from the irregularity of the deviations. The equation of state for hydrogen thus takes the form:

$$p=\frac{40.72T}{v-\delta}-\frac{39102}{(v-1.183)^2} \qquad [12a]$$

where

$$\log_{10}\delta=0.9831-\frac{1.26}{v}$$

in gram, atm., c.c. units.

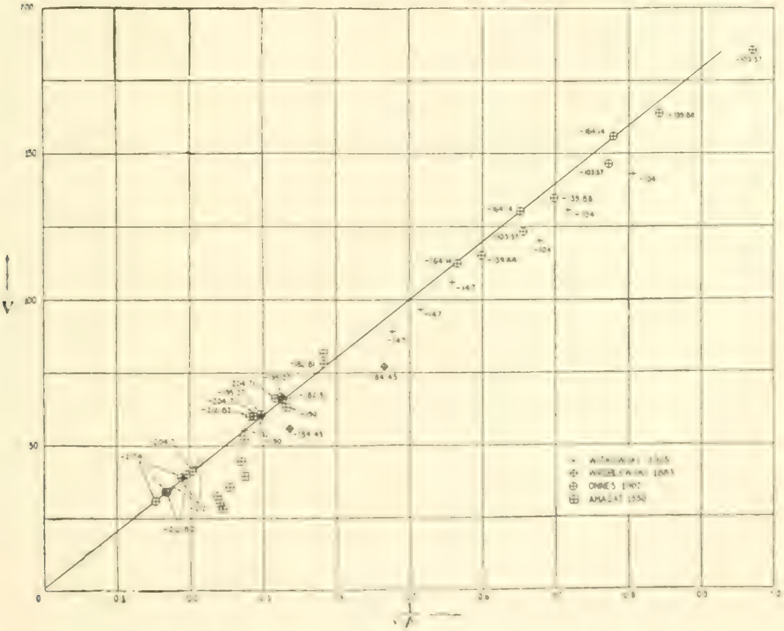

Fig. 3

Tables V and VI give a comparison of the pressures calculated from this equation of state with the observed pressures of Onnes and Braak,[21] Onnes, Crommelin and Miss Smid,[22] and Witkowski.[23] While the deviations are not large, seldom one per cent

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[21] Onnes and Braak, Leiden Comm., **100b** (1907).

[22] Onnes, Crommelin and Miss Smid, Leiden Comm., **146b** (1915).

[23] Witkowski, Krak. Anz. **305**, 1905.

### TABLE V
### Comparison of Observed and Calculated Pressures of Hydrogen Onnes and Braak[21] Onnes, Crommelin and Miss Smid[22]

| −217.40°C (−217.41) | | −204.69°C (−204.70) | | −183.18°C | | −139.88°C | | −103.57°C | | 0.00°C | | 20.00°C | | 100.20°C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| V. c.c. | P. Atms. | V. c.c. | P. Atms. | V. c.c. | P. Atms. | V. c.c. | P. Atms. | V. c.c. | P. Atms. | V. c.c. | P. Atms. | V. c.c. | P. Atms. | V. c.c. | P Atms. |
| 768.1 | *0.295<br>*0.295 | 7668. | *0.363<br>*0.363 | 177.5 | *20.40<br>20.54 | 216.2 | *25.43<br>*25.40 | 7705. | *0.896<br>*0.897 | 413.0 | *27.33<br>*27.39 | 190.1 | *65.25<br>*64.99 | 497.7 | *30.97<br>*30.98 |
| 142.4 | 14.64<br>15.11 | 159.6 | 16.75<br>17.01 | 146.5 | 24.71<br>24.87 | 163.6 | 33.77<br>33.71 | 214.0 | 32.99<br>32.90 | 318.6 | 35.60<br>35.58 | 170.5 | 73.08<br>72.74 | 388.8 | 39.80<br>39.83 |
| 122.5 | 16.79<br>17.41 | 129.8 | 20.46<br>20.78 | 127.5 | 28.37<br>28.58 | 134.6 | 41.27<br>41.14 | 178.8 | 39.66<br>39.54 | 262.6 | 43.41<br>43.38 | 161.6 | 77.36<br>76.95 | 3 0 | 50.25<br>50.30 |
| 107.9 | 18.86<br>19.60 | 109.7 | 24.02<br>24.46 | 111.6 | 32.42<br>32.72 | 115.0 | 48.56<br>48.34 | 143.2 | 49.90<br>49.66 | 226.4 | 50.58<br>50.52 | 154.3 | 81.19<br>80.73 | | |
| 39.24 | 46.42<br>47.83 | 72.66 | 35.49<br>36.28 | | | | | | | | | 147.5 | 85.13<br>84.43 | | |
| 34.34 | 52.90<br>53.36 | 66.47 | 38.64<br>39.49 | | | | | | | | | 142.4 | 88.38<br>87.79 | | |
| 31.00 | 58.97<br>58.00 | 60.29 | 42.44<br>43.31 | | | | | | | | | 136.1 | 92.68<br>91.31 | | |
| | | 41.31 | 61.92<br>61.87 | | | | | | | | | 131.1 | 96.49<br>95.76 | | |
| | | | | | | | | | | | | 126.4 | 100.34<br>99.54 | | |

* The observed pressure is given first, that calculated immediately beneath.

## TABLE VI

### Comparison of Observed and Calculated Pressures of Hydrogen

Witkowski[23]

| | −212°C | | −205°C | | −183°C | | −147°C | | −104°C | | −77°C | | 0°C | | 100°C | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P. Obs. Atms. | V. c.c. | P. Cal. Atms. | V. c.c. | P. Cal. Atms. | V. c.c. | P. Cal. Atms. | V. c.c. | P. Cal. Atms. | V. c.c. | P. Cal. Atms. | V. c.c. | P. Cal. Atms. | V. c.c. | P. Cal. Atms. | V. c.c. | P. Cal. Atms. |
| 1 | 2456 | 1.01 | 2747. | 1.008 | 3651. | 1.005 | 5132. | 1.001 | 6882. | 1.001 | 7189. | 1.002 | 11127. | 1.000 | 15200. | 1.000 |
| 10 | 238.7 | 10.16 | 269.9 | 10.11 | 365.2 | 10.01 | 515.7 | 10.00 | 693.0 | 9.995 | 804.3 | 9.940 | 1119. | 10.08 | 1527. | 10.00 |
| 20 | 114.9 | 20.55 | 131.9 | 20.36 | 181.9 | 20.09 | 259.3 | 19.53 | 349.1 | 19.96 | 405.1 | 19.95 | 563.0 | 19.97 | 767.2 | 19.99 |
| 30 | 71.1 | 30.95 | 86.03 | 30.72 | 121.2 | 30.11 | 173.9 | 29.91 | 234.5 | 29.89 | 272.1 | 29.88 | 377.6 | 30.01 | 513.9 | 29.91 |
| 40 | 51.1 | 41.32 | 63.61 | 40.95 | 90.91 | 40.13 | 131.3 | 39.72 | 177.3 | 39.78 | 205.6 | 39.80 | 284.9 | 39.89 | 387.2 | 39.97 |
| 50 | 42.9 | 50.90 | 50.60 | 50.82 | 72.90 | 50.05 | 105.8 | 49.63 | 142.9 | 49.64 | 165.7 | 49.60 | 229.2 | 49.82 | 311.3 | 49.91 |
| 60 | 35.8 | 59.83 | 42.16 | 60.32 | 61.09 | 59.80 | 89.03 | 59.34 | 120.1 | 59.46 | 139.1 | 59.41 | 192.5 | 60.55 | 260.3 | 59.87 |

the agreement is not as good as might be wished. In Fig. 4, the deviations of the calculated from the observed pressures are plotted for the Leiden data and those of Witkowski. The former are represented by dotted, and the latter by solid lines. For isotherms from + 100° to −140° the deviation increases fairly regularly, the calculated value being too small, and amounting to about one-half of one per cent at 60 atms. At lower temperatures the

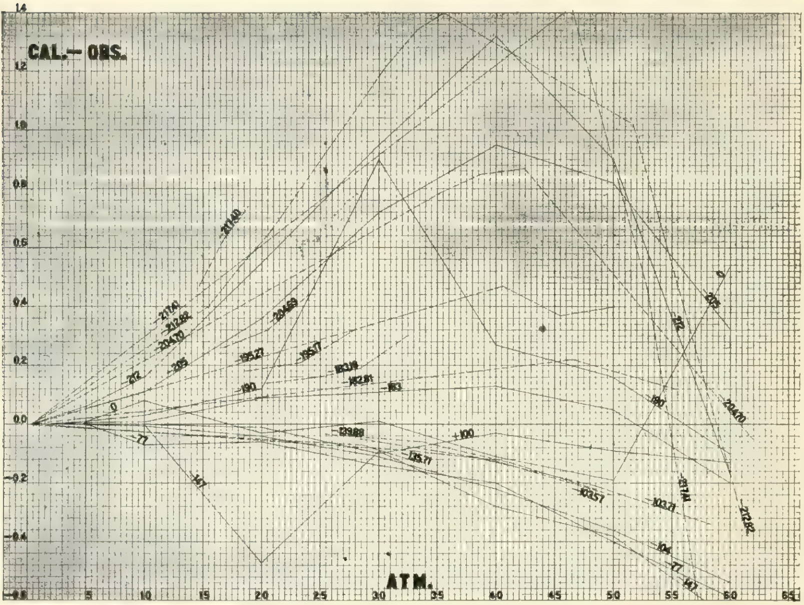

Fig. 4

deviations have the opposite sign and increase to a maximum (ca. 2%) at about 40 atms. and then rapidly decrease. The plot reveals much greater discrepancies in the data than were suspected by the observers. For example, at 20.5 atms. the deviation of the 204.69° isotherm differs from that of the 204.70° isotherm by 0.16 atm. Since these temperatures are the same within the limits of experiment, it follows that the observed pressures, at this particular point, differ by more than 0.5 per cent. Several other cases will be found as striking. The deviations are too inconsistent to surely indicate a fault in the values calculated by means of the equation of state. This inconsistency is further brought out in a comparison of calculated with observed values at extremely low temperatures. Table VII contains such a comparison, based on the data of Onnes and de Haas. Evidently, at temperatures very nearly the same and at the same volumes, the deviations of the calculated from the observed pressures in the various series are very different. Moreover, at such large volumes it seems improbable that the deviation from the perfect gas law is as great as the measurements indicate.

**TABLE VII**

**Comparison of Observed and Calculated Pressures of Hydrogen**
**Onnes and de Haas[24]**

| *−257.26°C* | | *−255.46°C* | | *−252.63°C.* | |
|---|---|---|---|---|---|
| *V.* *c.c.* | *P.* *Atms.* | *V.* *c.c.* | *P.* *Atms.* | *V.* *c.c.* | *P.* *Atms.* |
| 9603 | 0.06698* | 6514 | 0.10964* | 2338 | 0.34786* |
| | 0.06698* | | 0.10976* | | 0.36884* |
| 4829 | 0.13153 | 3415 | 0.20672 | 1315 | 0.60358 |
| | 0.13250 | | 0.20806 | | 0.64848 |
| | | 2520 | 0.27759 | | |
| | | | 0.28065 | | |
| | | 2225 | 0.31294 | | |
| | | | 0.31707 | | |
| | | 2223 | 0.31318 | | |
| | | | 0.31730 | | |

Another, and more direct, method is available for analyzing the data on hydrogen. This consists in determining the isometrics and for this purpose the pressures† have been calculated for a number of fixed volumes from the isothermal equations of Onnes. The isometrics so calculated are presented in Table VIII and Fig. 5. In each case a straight line seems best to represent the data. If we denote the equation of an isometric by

$$p = \psi T - \phi$$

the values of $\psi$ and $\phi$ obtained from the lines of Fig. 5 are given in Table IX.

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* The observed pressure is given first, that calculated immediately beneath.

†Pressures in atmospheres.

[24] Onnes and de Haas, Leiden Comm., **127c**, 1912.

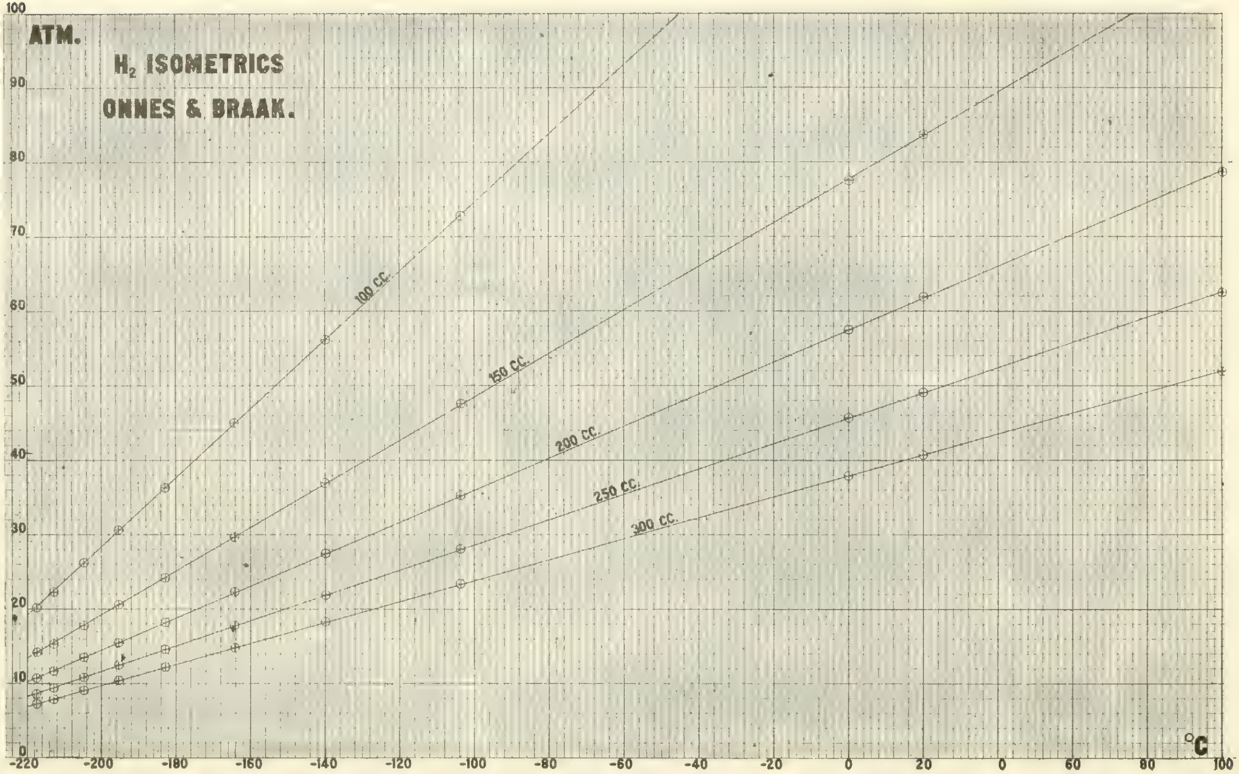
ATM.
$H_2$ ISOMETRICS
ONNES & BRAAK.
100
90
80
70
60
50
40
30
20
10
0
-220
-200
-180
-160
-140
-120
-100
-80
-60
-40
-20
0
20
0
60
80
100
°C
100 CC.
150 CC.
200 CC.
250 CC.
300 CC.

Fig. 5

### TABLE VIII

$H_2$ Isometrics. Onnes and Braak,[21] Onnes, Crommelin, and Miss Smid[22]

| *t°C* | *100 c.c.* | *150 c.c.* | *200 c.c.* | *250 c.c.* | *300 c.c.* |
|---|---|---|---|---|---|
| −217.41 | 20.169 | 14.216 | 10.659 | 8.631 | 7.252 |
| −212.82 | 22.324 | 15.309 | 11.663 | 9.432 | 7.906 |
| −204.70 | 26.212 | 17.776 | 13.465 | 10.841 | 9.074 |
| −195.27 | 30.622 | 20.588 | 15.526 | 12.466 | 10.415 |
| −182.81 | 36.329 | 24.235 | 18.205 | 14.585 | 12.167 |
| −164.14 | 45.032 | 29.744 | 22.275 | 17.805 | 14.818 |
| −139.88 | 56.179 | 36.933 | 27.531 | 21.949 | 18.251 |
| −103.57 | 72.767 | 47.561 | 35.348 | 28.131 | 23.363 |
| 0.00 | | 77.544 | 57.471 | 45.657 | 37.873 |
| 20.00 | | 83.662 | 61.896 | 49.127 | 40.730 |
| 100.20 | | | 78.743 | 62.537 | 57.863 |

Fig. 6a exhibits the deviations of the observed pressures from those calculated from the constants of the isometric equations presented in Table IX. It will be seen that the most representative line has been chosen in each case. The conclusion that the pressure is a linear function of the temperature at constant volume is

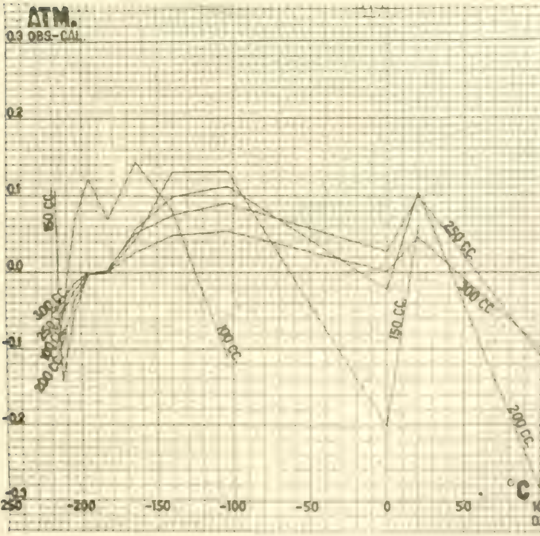

Fig 6a

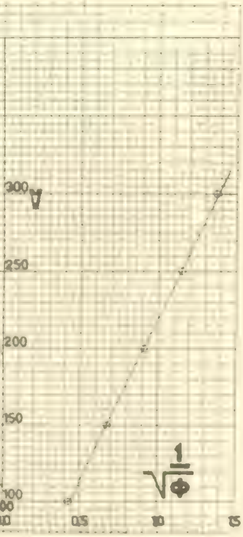

Fig. 6b

### TABLE IX

**Constants of the Isometrics of Hydrogen**

| *100c.c.* | | *150 c.c.* | | *200 c.c.* | | *250 c.c.* | | *300 c.c.* | |
|---|---|---|---|---|---|---|---|---|---|
| $\Psi$ | $\Phi$ | $\Psi$ | $\Phi$ | $\Psi$ | $\Phi$ | $\Psi$ | $\Phi$ | $\Psi$ | $\Phi$ |
| 0.46213 | 5.480 | 0.29270 | 2.200 | 0.21491 | 1.205 | 0.16983 | 0.756 | 0.14061 | 0.533 |

consequently at least not disproved, but supported, as far as the accuracy of the data are concerned. It thus becomes difficult to perceive how corrections to the constant volume hydrogen thermometer, deduced from the virial equation based on the same data, can represent a true fact of nature.

The constants of the equation of state can be found from the above isometrics for

$$\frac{R}{v-\delta}=\psi$$

and

$$\frac{A}{(v-l)^2}=\phi$$

The values of $\delta$ derived from the above isometrics are given below, compared with the corresponding values of $\delta$ calculated from the equation of state (12a). The variation of $\delta$ is too small to be detected within the limits of precision of the measurements, while the discrepancy between the two sets of values corresponds to an error in the volume of about 0.5 per cent, which is possible in view of discrepancies already indicated.

### TABLE X

**Values of $\delta$**

| | *100 c.c.* | *150 c.c.* | *200 c.c.* | *250 c.c.* | *300 c.c.* |
|---|---|---|---|---|---|
| From $\Psi$ | 11.88 | 10.88 | 10.52 | 10.19 | 10.39 |
| From Equa. 12*a* | 9.34 | 9.34 | 9.48 | 9.51 | 9.53 |

The volume plotted against $\frac{1}{\sqrt{\phi}}$ should give a straight line, from the constants of which $A$ and $l$ can be determined. This plot is represented in Fig. 6b. The values of $A$ and $l$ from the line there drawn are

$$A = 43600 \quad l = 10.2$$

Based entirely upon the Leiden data, the equation of state for hydrogen becomes

$$p = \frac{40.72T}{v - 10.5} - \frac{43600}{(v - 10.2)^2}$$

These constants, it is believed, may not be as reliable as those previously accepted for hydrogen. The coefficients of expansion and pressure increase of the gas will not, however, be appreciably altered if calculated with the new constants; but the corrections to the constant pressure hydrogen thermometer will differ from those computed by Buckingham from the Joule-Thomson data. The equation of state for hydrogen cannot be considered definitely established, but until more accurate data are available, equation (12a), given on page 263, can be regarded as best representing the facts.

A critical test of the validity of form of the equation of state, (12a), as well as of its constants, is obtained by calculating the Joule-Thomson coefficients of hydrogen and the inversion temperatures of the Joule-Thomson effect. These can then be compared with the values calculated by J. P. Dalton[25] from the hydrogen virial coefficients of Onnes.

The Joule-Thomson coefficient is defined by the equation

$$\mu = \frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{C_p}$$

while from the equation of state

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{(v-\delta)}{T}\left[\frac{1}{1 - \frac{2A}{RT}\frac{(v-\delta)^2}{(v-l)^3} - \frac{\alpha\delta}{v^2}}\right]$$

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[25] Dalton, Leiden Comm., **109a** (1909).

also
$$\left(\frac{\partial p}{\partial T}\right)_v=\frac{R}{v-\delta}$$

and
$$Cp=Cv+T\left(\frac{\partial p}{\partial T}\right)_v\cdot\left(\frac{\partial v}{\partial T}\right)_p=C_v+R\left[\frac{1}{1-\frac{2A}{RT}\frac{(v-\delta)^2}{(v-l)^3}-\frac{\alpha\delta}{v^2}}\right]$$

and finally
$$\mu=\frac{\frac{2A}{RT}\cdot\frac{v(v-\delta)^2}{(v-l)^3}-\delta\left(1-\frac{\alpha}{v}\right)}{Cv\left[1-\frac{2A}{RT}\cdot\frac{(v-\delta)^2}{(v-l)^3}-\frac{\alpha\delta}{v^2}\right]+R} \tag{13}$$

For values of $\mu$ at low pressures (13) reduced to
$$\mu=\frac{2A}{C_pRT}-\frac{\beta}{C_p} \tag{13a}$$

The inversion temperature, corresponding at $\mu=0$.
$$T_i=\frac{\frac{2A}{R}\cdot\frac{v(v-\delta)^2}{(v-l)^3}}{\delta(1-\alpha/v)} \tag{14}$$

**TABLE XI**
**Joule-Thomson Coefficient for Hydrogen at 1 Atm.**

| *T* <br> *°C* | *$\mu$ from [13a]* <br> *°C per Atm.* | *$\mu$, Dalton*[25] <br> *°C per Atm.* |
|---|---|---|
| −215 | +0.167 | +0.291 |
| −186 | +0.088 | +0.141 |
| −157 | +0.049 | +0.073 |
| −128 | +0.026 | +0.037 |
| −99 | +0.010 | +0.015 |
| −84.5 | +0.004 | +0.006 |
| −70 | −0.001 | −0.001 |
| −41 | −0.010 | −0.011 |
| −12 | −0.016 | −0.019 |
| +17 | −0.021 | −0.026 |

**TABLE XII**
**Inversion Temperature of Joule-Thomson Effect for Hydrogen**

| *Pressure Atms.* | *$T_i$, from [14] °C* | *$T_i$, Dalton*[25] *°C* |
|---|---|---|
| 1 | −73.2 | −72.6 |
| 10 | −75.9 | −74.1 |
| 20 | −78.3 | −75.8 |
| 50 | −85.7 | −81.9 |
| 100 | −99.0 | −91.7 |

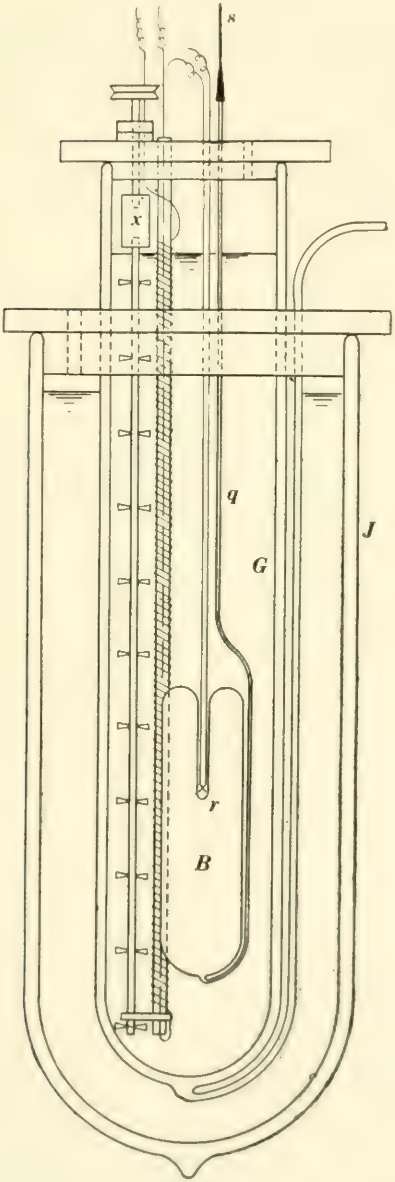

Fig. 7

A comparison of values computed fron (13a) and (14) with those found by Dalton is given in Tables XI and XII. In calculating $\mu$, $C_p$ has been assumed to have the constant value 3.41 cal. per gram, as was accepted by Dalton, in order to make the results comparable. In view of the rather involved computations by means of the virial equations the agreement may be considered satisfactory and lends support to the mathematical form of the equation of state.

## IV. Description of the Apparatus

### *The Bulb*

The bulb B (Fig. 7) is of fused quartz, 135 mm. long and 33 mm outside diameter. The thickness of the walls is approximately 0.75 mm. During the earlier experiments a reëntrant tube *r*, about 3 mm. in diameter and 45 mm. long was provided at the top of the bulb to receive a thermocouple. The bottom of this tube was finally fractured, owing to the freezing of a small amount of water which condensed therein on standing over from a previous experiment. In repairing the bulb the reëntrant tube was removed, as it had not been found altogether satisfactory. The volume of the first form, with reëntrant tube, was 91.31 c.c. at room temperature. The volume of the present bulb is 91.86 c.c. At the bottom of the bulb there is fused a quartz capillary, *q*, fashioned in the manner shown, which extends above the top of the vessel containing the bath. The end of the quartz capillary is ground into a conical steel cap and cemented with de Khotinsky cement. A silver capillary is soldered into the upper end of this cap and serves to connect the bulb with the manometer. The length of the quartz capillary is 50 cm. and its volume 0.00316 c.c. per cm. The bulb is supported by means of a quartz rod, *Q* (Fig. 12), fused to its top and which is cemented into a brass collar screwed to the cryostat cover.

The choice of fused quartz as bulb material rests mainly upon its small coefficient of thermal expansion and its supposedly less tendency to adsorb gases. If glass were used, its thermal expansion would have to be known very accurately. The values of the coefficient of expansion of quartz were taken from an analysis of the existing data by R. S. Taylor and L. B. Smith[26] of this laboratory.

The following relation was used for the true linear temperature coefficient of expansion, $\lambda$, of quartz below 0°C.:

$$\log_{10}(\lambda\times10^7+19)=1.5414-\frac{50.789}{T}$$

Quartz exhibits a maximum density at about $-80$°C. and its mean coefficient of expansion passes through zero at $-148$°C. This property makes it especially desirable as a thermometric gas container at low temperatures.

The change in volume of the bulb with pressure was determined as follows. The bulb and a portion of the quartz capillary were filled with water and placed in a horizontal position. The capillary was then connected through a three-way stopcock to a vertical tube and the latter partly filled with mercury, the lower end of the mercury being in contact with the surface of the water in the capillary. The length of the mercury column was then increased, and the displacement of the contact surface between the mercury and water noted. The volume per unit length of the capillary being known, the change of volume with pressure could be determined after making a correction for the compressibility of the water. By means of the three-way stopcock, the excess of mercury could be drained from the apparatus and the experiment repeated. The mean of four such measurements gave the pressure coefficient of the bulb as .0110 c.c. per atm. ± 0.0003. The figure given by Chappuis[27] for the quartz bulb used by him is 0.00444 c.c. per atm., reduced to the same volume. It is probable that th difference is due to the thinner walls of the thermometer bulb.

[26] This will be published in a forthcoming paper on the density and vapor pressure of ether at low temperatures. The papers consulted in connection with the thermal expansion were:

Holborn and Henning, Ann. der Phys. **10**, p. 446, 1903.
Scheel and Chappuis, Wiss. Abh. Phys. Tech. Reichsanstalt, **4**, p. 54, 1904.
Harlow, Proc. Roy. Soc. Lond., **24**, p. 30, 1912.
Henning, Ann. der Phys. **22**, p. 606, 1907.
Scheel and Dorsey, Phys. Rev. **27**, p. 101, 1907.
Randall, Phys. Rev., **3a**, p. 216, 1910.

[27] Chappuis, Trav. Mem. Bur. Inst., **6**, 1888.

### *The Connecting Capillary*

The internal diameter of the silver capillary, connecting the bulb with the manometer, was determined from measurements of its length, weight, and external diameter: the density of the silver being taken as 10.5. The internal diameter thus found was 0.457 mm. The length of this connection is 144 cm. and its volume consequently 0.00164 c.c. per cm.

The lower end of the silver capillary connects with a capillary of glass, *g* (Fig. 8), 15 cm. long, which is cemented into the steel cap, *k*, of the short manometer tube. The introduction of this glass capillary is a safeguard to prevent mercury from reaching the silver tube should the level inadvertently be raised above the contact point. It served this purpose on two occasions.* The volume of the glass section was found to be 0.296 c.c.

### *The Manometer*

The manometer tubes, *C* and *C′* (Fig. 8), are of pyrex glass specially selected for uniformity of bore and straightness, their internal diameter being 15 mm.† The tubes are fastened into the wells of the manometer base *D* through rubber stoppers forced tight by means of the brass clamps *d*. The long tube is supported near the top by a centering device on the cover plate of the manometer frame *A*. The under side of the short tube cap *k* is provided with a steel needle point 0.3 mm. long. This detail is shown in the enlargement. Exact contact between the point and the mercury meniscus is determined by placing the gap in series with a small electromagnetic interrupter and telephone receiver. The long tube is connected to a vaccum pump and maintained exhausted, so that the indications are independent of barometric pressure.

The manometer base *D* is of steel 20×10×10 cm. It is screwed to a steel leveling stand *L* (Fig. 10), the whole resting on two massive blocks of slate. The manometer tubes are connected by a

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* A small valve could of course be used instead; but this seemed an unnecessary complication and one almost surely destined to provide trouble.

† The tubes were calibrated for bore and the correction for capillary depression was found to be negligible.

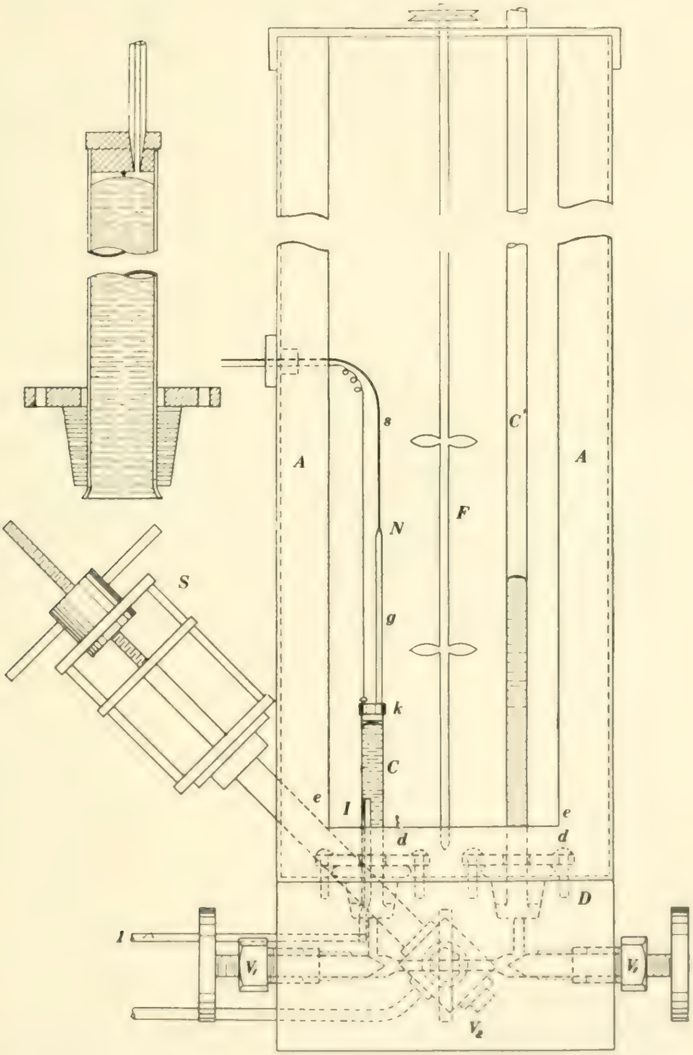

Fig. 8

passage 1.6 mm. in diameter. A second passage at right angles to the first and half way between the tubes makes connection with the mercury reservoir.

Each manometer tube is provided with a shut-off valve $V_1$. The valve details are shown in Fig. 9. In closing the valve the piston $P$ moves forward without rotation, thereby preserving the packing from loosening. The end of the piston is cup-shaped, $l$, and its taper is 0.5° less than that of the seat. In this way a firmer seating is realized than with the ordinary form.

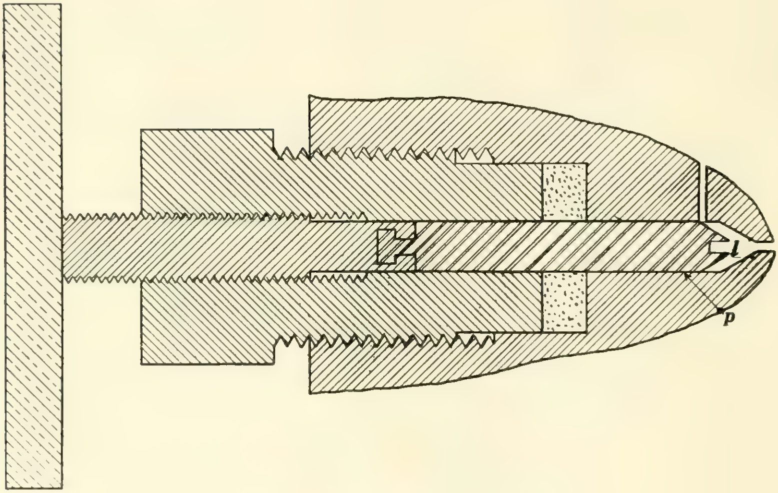

Fig. 9

The mercury reservoir, an ordinary lift-bulb mounted between vertical guides, connects with the manometer base through the rubber pressure tubing $R$ (Fig. 8) and the shut-off valve $V_2$. The steel block containing this valve is threaded into the base and made tight with an aluminum washer. The reservoir is used only for rough adjustment of the mercury level. The valve $V_2$ is then closed and fine adjustment made by means of the injector *S*. One turn of the handle raises the level of the mercury in the short tube about 0.04 mm.

The frame *A* of the manometer is fashioned from an iron channel section. The section was cut at the corners *ee*, bent into a *U* form and the corners welded. The bottom and faces were planed smooth. It is fastened to the base by screws and made tight by an impregnated paper gasket. Sheets of plate glass are screwed to front and back. These faces were made water-tight with heavy shellac and the outer edges sealed with litharge and glycerin cement. A stirrer, *F*, provides circulation of the bath liquid, the temperature of which is given by a calibrated Baudin thermometer *t* (Fig. 10) graduated to 0.1°C.

Kerosene was used as a bath liquid during the greater part of the measurements. The rubber stoppers seating the manometer tubes were covered with a thick layer of shellac to prevent their disintegration. After more than a year's use the kerosene finally reached the stoppers and they had to be replaced. Thereafter water was used instead of kerosene. The interior surfaces of the frame and the base were covered with red lead paint to prevent rusting and then painted white to improve the illumination of the columns.

Gas is admitted to the bulb through the tube *I* (Fig. 8). The mercury is allowed to fall below the upper end of *I*, the tube now remaining filled with mercury back to the stopcock 1 (Fig. 10). This is drained out into the trap *T*. When the bulb has been loaded the mercury is allowed to ascend in the short manometer tube and the inlet tube is again filled with mercury back to 1.

### *The Cathetometer*

The difference in level of the fixed point and the column in the long tube was measured with a Gaertner cathetometer. This instrument possesses a steel scale which was compared with a Gaertner standard meter (No. 1768) calibrated by the Bureau of Standards. The scale error was found sensibly constant and amounted to 0.00002 cm. per cm. Taking the coefficient of expansion of steel to be $11\times10^{-6}$, the scale correction is given by the following formula:

$$H_{cor.}=H_{obs.}[1+11\times10^{-6}(t-20)+20\times10^{-6}]$$

The instrument is fitted with a micrometer screw attachment by which 0.01 mm. can be read and 0.001 mm. estimated. With practice it was found that successive readings deviated by not more than a few thousandths of a millimeter.

### *The Cryostat*

The thermometer bulb is mounted in the form of cryostat shown in Fig. 7. The inner vessel *G*, containing the bath, is of pyrex glass and double-walled. The space between the walls is connected to the vacuum pump and can be exhausted to any desired degree. The length of this vessel is 40 cm. and its internal diameter 6.7 cm. It is closed by a cover of asbestos wood. To this cover are attached a heater and a stirrer; the resistance wire of the heater being wound on a glass rod with asbestos string insulation between the windings. To minimize heat conduction a vulcanite section *x* is placed in the stirrer shaft just beneath the cover. The bath vessel is cemented with de Khotinsky cement into the asbestos wood cover of the outer Dewar tube *J*. This latter is 40 cm. long with an internal diameter of 13.5 cm. The outer vessel, and also its cover, bearing the inner vessel, are mounted in vertical guides between the surfaces of a double-decked table. For the bath liquid normal pentane was used, which remains quite liquid down to −145°C. For comparisons below this point the thermometer was immersed directly in liquid air or oxygen.

The outer vessel being filled with liquid air, maintained at a fairly constant level, the temperature of the bath can readily be held constant at any desired point by suitably regulating the heating current and the degree of exhaustion within the walls of the bath vessel. In practice, the walls are pumped out to the right degree as determined by experiment and the temperature control during the observations effected solely by hand regulation of the heater current. Over a period of fifteen or twenty minutes the temperature can be held to the same value within 0.01°C.

### *Auxiliary Apparatus*

Fig. 10 illustrates the general arrangement of the apparatus. *M* represents a supply of helium, *K*, a hydrogen generator, and when nitrogen was used it was introduced at *E*. A Toepler pump *N* served to transfer the helium from its container to the gas reservoir *O*. In the cases of hydrogen and nitrogen, where fresh gas could be generated whenever needed, the Toepler pump was not used, the reservoir being filled directly from the generator. *U* is a carbon adsorbing tube to be immersed in liquid air in purifying the helium. The gas could be circulated repeatedly through the purifying tube by means of the pump. *H* is an auxiliary lift pump for convenience in loading the thermometer. Before entering the bulb the gas passed through the purifying tube *W* containing soda lime and phosphorus pentoxide and the

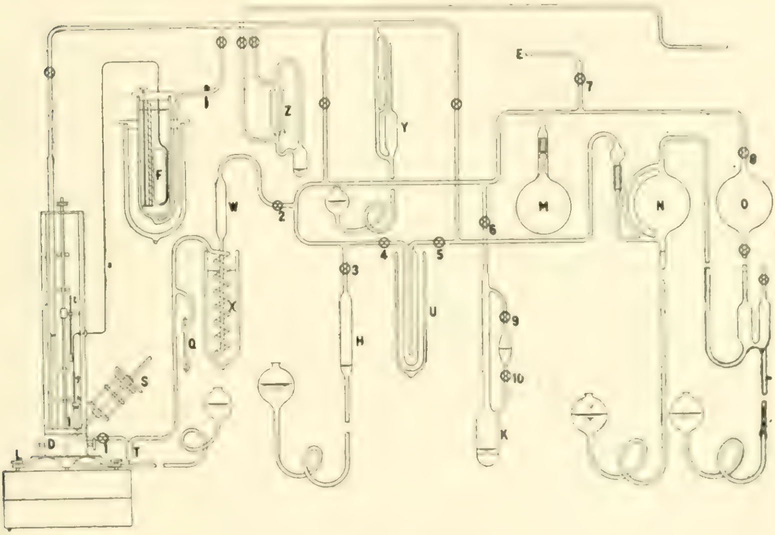

Fig. 10

spiral X immersed in liquid air. A Geissler tube $Q$ served as means of checking the purity of the gas. At $Y$ and $Z$ are shown a McLeod gauge and mercury diffusion pump. The latter is backed up by a rotary oil pump capable of giving 0.01 mm. With the two in series the apparatus could be exhausted to better than $1 \times 10^{-5}$ mm.

## V. Sources of Error

The three main sources of error in gas thermometry involve the control of the volume of the bulb, the volume and temperature of the dead space, and the temperature of the mercury columns. For the present it is assumed that the total mass of the thermometric gas exists only in the gas phase, and we reserve for discussion in another place, the error which may result from adsorption of the gas on the walls of the bulb at low temperatures.

Assuming that it is desired to measure a temperature of $-100°$ C., it is possible to forecast the accuracy with which this can be accomplished. The actually observed pressure can be measured to 0.01 mm. The corrections for temperature expansion of the cathetometer scale and the reduction of the mercury column to standard gravity can be made with sufficient accuracy to introduce no appreciable error. If the recorded pressure is about 500 mm. the correction for temperature of the mercury columns (ca. 25°C.) is of the order of 2.5 mm., which must be known to 0.2 per cent and the coefficient of expansion of mercury together with the mean temperature of the manometer must each be known to 0.14 per cent. Use was made of the coefficient of expansion of mercury given by Callendar and Moss.[28] The mean temperature of the manometer must then be known to ±0.03°C. The necessity of jacketing the columns, therefore, is apparent. The usual procedure of placing two or three thermometers along the column in air is believed to be inadequate. With the columns immersed in a stirred bath of kerosene or water, the temperature of which is given by a calibrated thermometer readable to 0.01°C., we feel hat the necessary condition of determining the average temperature to 0.03° is certainly fulfilled. The correction for difference in level of the bulb and contact point only amounts to one or two hundredths of a millimeter and can be accurately applied. The dead space correction at the ice point amounts to about 0.04 mm. and at −100°C. to 1.5 mm. This correction should then be known to 0.2 per cent in order to introduce no further error. It follows that the temperature of the dead space should be known to ±0.1°C. and its volume to 0.14 per cent. Both these conditions can be realized. Thus the pressures, $p_0$ and $p$, can be determined in the case under consideration to 0.01 mm. or about 1/50,000.

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[28] Callendar and Moss, Phil. Trans., 1911. $\alpha = 0.000180555 + 0.0_7 1244t + 0.0_{10} 254t^2$.

The correction term for change in volume of the bulb must be accurate to about ten per cent in the case of fused quartz, if the precision previously laid down is to be maintained. If a glass bulb is used, the necessary precision of this term would be of the order of one per cent, which for glass would be very difficult to realize and much uncertainty has undoubtedly been introduced into gas thermometry because of the uncertainty of the expansion data. In the case of quartz, both the thermal expansion and that due to pressure can be determined easily with the necessary precision. It thus appears that the bracketed term of the temperature formula (3) can be determined to 1/20,000 under the conditions assumed.

We now have the temperature given as the product of three factors, $\overset{t}{\underset{0}{\epsilon}}$, $p_0$, and the bracketed term. The estimated precision of these three quantities is 1/12,000, 1/60,000, and 1/20,000 respectively. The percentage error in the temperature can thus be put at 0.01 per cent. Hence, at −100°C. the temperature is determinable to ±0.01°C. At the boiling point of oxygen, we believe the limit of our present accuracy to be ±0.02°C.

## VI. Description of the Experiments

### A. *Indirect Determination of the Dead Space Volume*

The volume of the dead space could be directly measured with the exception of that part comprised between the level of the contact point and the mercury meniscus. This cannot be sufficiently accurately calculated on the assumption that the meniscus is a segment of a sphere. Moreover, the ellipsoidal formula used by Travers, Senter and Jaquerod[29] is not in agreement with that used by Chappuis,[27] based on the work of Desains. These two formulæ applied to our case and comprising the volume between the under surface of the steel cap *k* and the meniscus gave 0.159 c.c. and 0.175 c.c. respectively. Since the more recent measurements of Scheel and Heuse[30] upon meniscus volumes were not known at the time, it was decided to determine the volume experimentally by an indirect method.

Assuming the coefficient of pressure increase of air to be given correctly by calculation from the equation of state, the volume of the dead space could be found after determining the ice and steam points on the gas thermometer; since it would then be the only unknown quantity. A description of the procedure in determining ice and steam points will be given in the next section. It will suffice here to record the dead space volume thus found. On taking the contact space volume to be 0.196 c.c., we have the following measurements of the coefficient of pressure increase of air:

Air. $p = 607.88$ mm.

| $\overset{100}{\underset{0}{\epsilon_v}}$ | *Date* |
|---|---|
| 0.0036682 | 1/21/21 |
| 0.0036691 | 1/24/21 |
| 0.0036689 | 1/29/21 |
| $0.0036687 \pm 0.0_63$ mean. | |

The value calculated from the equation of state is 0.0036690.* Subsequently, the experimental results of Scheel and Heuse have come to light and applying these data to the dimensions of the contact space there is found 0.197 c.c. The agreement is astonishingly close in view of the involved manner in which the volume 0.196 was deduced and furnishes evidence of the accuracy of the apparatus and procedure.

The total volume of the dead space is 0.886 c.c. The ratio of dead space to bulb is thus 0.0097. This is larger than might be desired; but inasmuch as 60 per cent of the dead space is within the manometer, where its temperature is accurately known, the dead space correction, though fairly large, is calculable with considerable exactness.

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* $\overset{100}{\underset{0}{\epsilon_v}} = 0.00366118 + 129 \times 10^{-10} p_0$ (mm.)

[29] Travers, Senter and Jaquerod, Phil. Trans. **200,** p. 110, 1903.

[30] Scheel and Heuse, Ann. der Phys., **33,** p. 291, 1910.

### *B. Coefficient of Pressure Increase of Nitrogen*

As a test of the operation of the apparatus and of the value determined for the dead space volume, $\overset{100}{\underset{0}{\epsilon_v}}$ for nitrogen was next determined. This could be then compared with the value calculated from the equation of state.

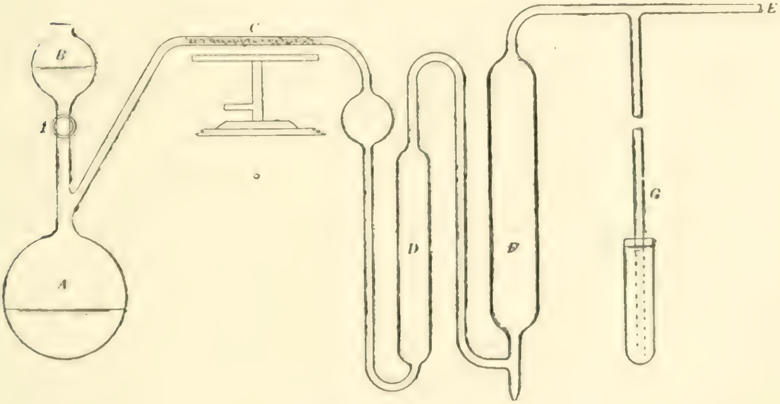

Fig. 11

The nitrogen was prepared in the usual manner by the interaction of ammonium sulphate and sodium nitrite. The generating train is shown in Fig. 11. A solution of 70 grams of $NH_4SO_4$ in 120 c.c. of water was placed in *A*. *B* contained a solution of 40 grams of $NaNO_2$ in 50 c.c. of water. The nitrite could be admitted gradually into *A* through the stopcock 1, the vessel *A* being warmed in a water bath. The reaction is autocatalytic, and if the temperature is not controlled, proceeds with too great rapidity. The gas passed over heated copper in the quartz tube *C* and then through sulphuric acid in *D* and phosphorus pentoxide in *F*. The tube *G*, dipping into mercury, acted as a safety valve. The generating train was connected to the rest of the system at $E$ (Fig. 10). Before preparing the gas the whole system was pumped out and repeated rinsing with the gas preceded the final exhaustion and filling of the reservoir $O$. The pressure within the reservoir could be read by means of the mercury column $J$.

The reservoir having been filled with nitrogen at about one atmosphere pressure, the generating train was now shut off at 7 and the rest of the system completely exhausted. Stopcocks 4 and 5 were kept closed, the carbon purifying tube being used only in the case of helium. By lowering the mercury in the short manometer tube below the gas inlet and allowing the mercury in the inlet passage to flow into the trap $T$, the bulb could be placed in communication with the pump through the stopcock 2. The bulb was maintained at 360°C. within an electric heater and exhausted to 0.0001 mm. at this temperature. A small amount of gas was now introduced and after standing a few minutes again pumped out. This rinsing process was repeated four or five times before the bulb was allowed to cool and finally loaded. In adjusting the pressure to the desired amount the lift pump $H$ was of use. Gas could be admitted into $H$ from the reservoir and then after closing 8 could be pushed over into the bulb. During the filling the coil $X$ was cooled by liquid air to remove any condensible constituents. Examination of the spectrum of the gas in the Geissler tube $Q$ furnished satisfactory evidence of its purity.

To determine the ice point the bulb was placed in a large Dewar tube and surrounded with shavings of distilled water ice. Ice cold distilled water was added, immersing the bulb to a depth of two or three inches. The dead space volume was considered in two parts — one at the temperature of the manometer; the other, comprised between the top of the bath and the cover, at the mean temperature of room and bath. In reading the pressure four observations of the height of the fixed point* and of the mercury in the long column were taken. During any run the maximum deviation was not greater than 0.01 mm. The ice points before and after the steam points were found to be:

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* The fixed point did not vary during any given run; but its height was found to depend slightly upon the pressure of the gas, due presumably to a small amount of give in the rubber seating of the tube.

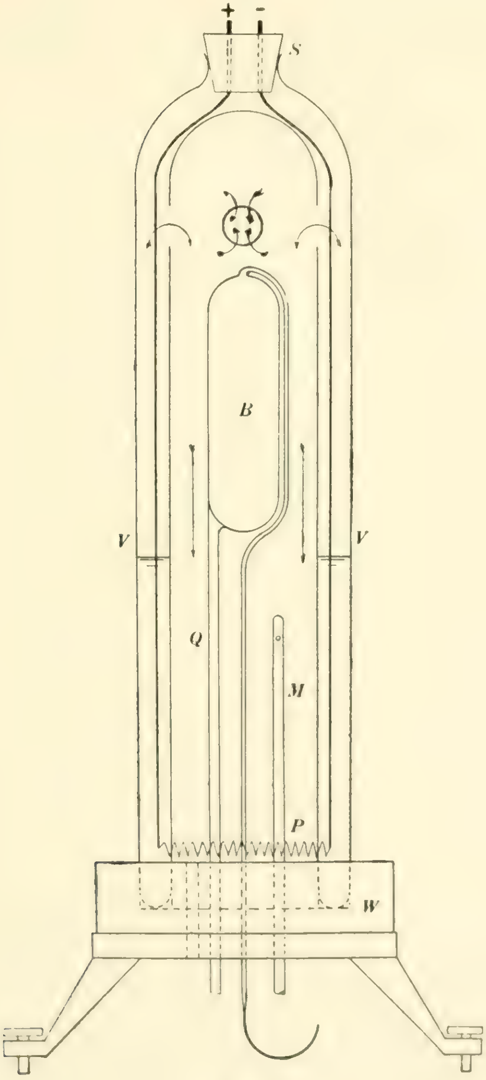

Fig. 12

| *Ice Point, $N_2$*<br>*mm.* | *Date* |
|---|---|
| 653.80 | 3/18/21 |
| 653.82 | 4/20/21 |

The steam point was determined in a specially designed boiler, illustrated in Fig. 12. The double-walled vessel *V* is of pyrex glass, 40 cm. long and 6.7 cm. internal diameter. Distilled water is placed in the annular space and is heated by a platinum coil *P* immersed directly in the liquid. The Monel lead wires are brought out through the stopper *S*. The steam passes through the openings *A* and down over the bulb, issuing through an opening in the asbestos wood base *W*. The whole is mounted on a brass leveling stand. A glass tube *M* connects with a U-tube water manometer to indicate the excess of steam pressure over atmospheric. When in use, a pipe cover is slipped down over the vessel for insulation. This type of boiler was found to give excellent results, the water boiling gently and continuously and the steam pressure not more than one millimeter of water above that of the atmosphere. The readings were found independent of the rate of boiling within wide limits.

Three steam points were taken with the nitrogen filling as follows:

| *Steam Point, $N_2$*<br>*mm.* | *Temperature*<br>*°C.* | *Date* |
|---|---|---|
| 895.06 | 100.62 | 3/23/21 |
| 894.91 | 100.57 | 3/23/21 |
| 894.39 | 100.34 | 3/24/21 |

The values for $\overset{100}{\underset{0}{\epsilon}}{}_v$ from the mean of the ice points and each steam point are given in the first column of Table XIII. The value calculated from the equation of state* and that given by Henning and Heuse[31] are also given for comparison.

The difference between our measured value and that calculated from the equation of state amounts to 1/7350. The calculated

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* For $N_2: = 0.00366118 + 121 \times 10^{-10} p_0$ (mm.).

[31] Henning and Heuse, Zeit. f. Phys., **5**, p. 285, 1921.

TABLE XIII

**Coefficient of Pressure Increase for Nitrogen**

$p_0 = 653.81$

| *Measured* $\times 10^7$ | *Calc., Keyes** $\times 10^7$ | *Measured, Henning and Heuse* [31] $\times 10^7$ |
|---|---|---|
| 36698<br>36693<br>36698<br>36696 mean. | 36691 | 36692 |

value we believe the more nearly correct, especially in view of its agreement with the measurements of Henning and Heuse. It was proposed in measuring temperatures to utilize the calculated values of the coefficients and the above measurements were a test of the sufficiency of the apparatus. We believe that in general a precision of 1/10,000 is realizable.

### C. *The Diffusion of Helium and Hydrogen Through Quartz*

It was originally contemplated to use helium as thermometric gas. To this end the helium in the globe $M$ (Fig. 10) — furnished in a high state of purity by the Linde Air Products Co. of Buffalo — was transferred to the reservoir $O$, being circulated repeatedly through the charcoal tube $U$ immersed in liquid air. The thermometer bulb was loaded to an ice-point pressure of about 621 mm.

As soon as measurements were undertaken it became apparent that gas was being lost from the bulb. In two days the ice point dropped from 620.74 mm. to 619.29 mm., the bulb remaining at about 27°C. during the interval. The pressure inside being less than atmospheric, the possibility of leakage was excluded. It was known that helium diffuses readily through quartz at high temperatures[32], but such a large effect at ordinary temperatures had not been suspected. The rate of diffusion at 27°C. and 682 mm. internal pressure was found to be 0.03 mm. per hour. At 100°C. the rate appeared nearly ten times as great. Subsequently we have read of a similar experience of Henning,[33] who found the rate of diffusion at room temperature and 700 mm. internal pressure to be 0.01 mm. per hour in the case of the bulb used by him.

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[32] Jaquerod and Perrot, C. r., **139,** p. 789, 1904.

[33] Henning, Zeit. f. Phys., **5,** p. 264, 1921.

* For $N_2$: $= 0.00366118 + 121 \times 10^{-10} p_0$ (mm.).

On account of the rapid decrease in the rate of diffusion with lowering of the temperature it seems probable that it would become negligible at 0°C. If the bulb of the thermometer were not heated above this point it might be possible to utilize the attractive combination of helium in quartz for the measurement of low temperatures; but owing to the difficulties of this procedure the use of helium in the present instance was discarded.

Hydrogen was the next choice. It was prepared by the action of pure sodium amalgam upon water in the type of generator shown at $K$ (Fig. 10). The small bulb in the side tube contained air-free water which could be admitted at will into the lower bulb containing the amalgam. The hydrogen was dried in the process of loading by passing through the pentoxide tube $W$ and the spiral $X$.

Diffusion of the gas through the walls of the bulb was again found, although to a much less extent than in the case of helium. The ice-point pressure of the initial loading was 645.11 mm. A succession of steam points gave lower pressures each time, the drop amounting to 0.4 mm. in four days. An estimate of the rate of diffusion at any definite temperature cannot be given, it being only possible to conclude that at 100°C. it is considerably greater than 0.004 mm. per hour.

The possibility of using hydrogen in quartz is by no means excluded, although the rate of diffusion at 100° is large enough to cause some difficulty in determining the coefficient of pressure increase. It had been decided, however, to employ nitrogen also in the investigation and with this gas diffusion causes no trouble. Later a comparison was made with the hydrogen thermometer.

### *D. Measurements with the Nitrogen Thermometer*

### *Thermocouple Calibration*

With the nitrogen thermometer a calibration was made of a multiple copper-constantan thermocouple down to the boiling point of oxygen. The thermocouple consisted of six copper-constantan couples in series, each wire of No. 30 B. & S. gauge. The junctions were silver soldered by bringing a tiny drop of molten silver solder into contact with the junction, thus avoiding direct heating of the wires with the blow pipe flame. Each lead was covered with bakelite varnish and baked at 100°C. for several hours. They were further insulated from each other with silk floss and then tied together with silk thread to form a pencil three millimeters in diameter and five centimeters long. The "cold junction" was kept in ice within a small thermos bottle. The "hot junction" could be introduced into the reëntrant tube of the thermometer bulb. With this arrangement there seemed no doubt that the temperature of the indicating junction and that of the gas within the bulb would be the same.

The electromotive force of the thermocouple was measured on a Leeds and Northrup Type K potentiometer in conjunction with a high sensibility galvanometer of seventeen ohms internal resistance. The whole electrical system was placed on interconnected metal plates in order to be shielded from surface leakage due to external potential differences.[34] Very little trouble was experienced from leakage effects except during one period of extremely damp weather when measurements had to be suspended. The indications of the thermocouple were reproducible to one microvolt.

The first calibration was made at twelve temperatures ranging from −18.33°C. to −183.39°C. on the nitrogen scale. A check calibration at −183.15°C. was made two months later, and after a further period of three months, another calibration was undertaken in the range −51.12°C. to −130.54°C. This latter calibration furnished a very good check on the reliability of the gas thermometer and the constancy of the thermocouple, for it was made under quite different conditions. The quartz thermometer bulb had been broken during the intervening period and in its new form was without the reëntrant tube. The individual junctions of the thermocouple had, moreover, been separated and each protected by a thin tube of glass. They were then equally spaced about the circumference of the bulb. The ice-point pressure of the nitrogen thermometer at this time was somewhat higher, 727.88 mm., being a new loading. The results were in very satisfactory agreement with the first calibration, the maximum deviation being 0.04°C. It would thus appear that a properly prepared

[34] W. P. White, J. Am. Ch. Soc., **36**, p. 2011, 1914.

and protected copper-constantan thermocouple furnishes a satisfactory and reproducible method of measuring low temperatures, at least down to −183°C. To increase its applicability there ought to be a number of reliable fixed points in the low temperature range. The second part of this paper will give determinations of the freezing points of certain organic compounds with this purpose in view.

The relation between temperature and electromotive force of the couple employed was found to be represented with a maximum error of 0.18°C. by the following formula:

$$E = 0.1486(t)^{2.137} - 222.20\,t \tag{15}$$

With the exception of the range from −37° to −91° the deviation of the values calculated from this formula from those actually observed is nowhere greater than 0.05°C. The relation can thus be used to calculate temperatures from observed electromotive forces when supplemented by a deviation plot. The data on the calibration of the thermocouple are set forth in Table XIV. The last column shows the deviations of the actually observed tem-

**TABLE XIV**
**Thermocouple Calibration**

$$e_c = 0.1486t^{2.137} - 222.20t$$

| *Date* | *Pressure* | | | | | | |
|---|---|---|---|---|---|---|---|
| | $P_o$ *mm.* | $P_t$ *mm.* | $t_{N_2}$ °*C* | *E. M. F. Observed* $10^{-6}$ *volts* | *E. M. F. Calculated* $10^{-6}$ *volts* | $E_{cal.} - E_{obs.}$ $10^{-6}$ *volts* | $t_{cal.} - t_{obs.}$ °*C* |
| 4/29/21 | 653.83 | 609.85 | − 18.33 | 3998 | 3999 | + 1 | +0.005 |
| 5/ 2/21 | 653.83 | 583.66 | − 29.26 | 6303 | 6300 | − 3 | −0.014 |
| 5/ 2/21 | 653.83 | 562.23 | − 38.19 | 8121 | 8129 | + 8 | +0.041 |
| 4/29/21 | 653.83 | 539.54 | − 47.65 | 9992 | 10015 | +23 | +0.117 |
| 4/29/21 | 653.83 | 507.59 | − 60.97 | 12544 | 12578 | +34 | +0.177 |
| 4/27/21 | 653.83 | 468.54 | − 77.25 | 15530 | 15556 | +26 | +0.146 |
| 4/28/21 | 653.83 | 424.93 | − 95.43 | 18674 | 18678 | + 4 | +0.024 |
| 4/29/21 | 653.83 | 370.49 | −118.11 | 22254 | 22258 | + 4 | +0.027 |
| 4/28/21 | 653.83 | 345.37 | −125.58 | 23785 | 23791 | + 6 | +0.041 |
| 4/28/21 | 653.83 | 325.62 | −136.82 | 24941 | 24944 | + 3 | +0.022 |
| 5/ 2/21 | 653.83 | 213.88 | −183.39 | 30542 | 30543 | + 1 | +0.010 |
| 7/ 8/21 | 654.04 | 214.52 | −183.15 | 30518 | 30518 | 0 | 0 |
| 10/14/21 | 727.88 | 591.37 | − 51.12 | 10671 | 10693 | +22 | +0.113 |
| 10/14/21 | 727.88 | 520.17 | − 77.77 | 15627 | 15649 | +22 | +0.124 |
| 10/14/21 | 727.88 | 451.90 | −103.33 | 19959 | 19965 | + 6 | +0.037 |
| 10/14/21 | 727.88 | 379.17 | −130.54 | 24072 | 24071 | − 1 | −0.007 |

peratures from those calculated by means of formula (15). The temperatures are those given by the nitrogen thermometer. In subsequent measurements with the thermocouple the temperatures were corrected so as to be in accord with the indications of the hydrogen thermometer.

### *Platinum Resistance Thermometer Comparison*

The platinum resistance thermometer was compared with the nitrogen thermometer over the range −30°C. to −183°C. The resistance thermometer was of the flat Dickinson and Mueller type with silver sheath and steel stem of 0.010 inch wall thickness. Its resistance was measured on a Mueller dial bridge made by Wolff. The bridge coils were immersed in a stirred bath of kerosene, a thermostatic device keeping the temperature constant to ±0.03°C. No measurable heating effect of the thermometer current was detected and the galvanometer responded to changes in temperature of one or two thousandths of a degree. The ice-point resistance was found to be 25.5370 ohms, the fundamental interval 9.9606 ohms, and $\delta$ 1.51. This latter was determined from readings on the boiling point of naphthalene $[217.96° + 0.058(p - 760)]$.[35] The ice point did not shift by more than five or six ten-thousandths of an ohm during the period of several months the resistance thermometer was in use.

The results of three comparisons are given in Table XV. The general form of the deviation of the Callendar formula from the gas scale is similar to that found by Henning;[36] but the actual deviations at low temperatures are considerably less. Thus at −183°C. the platinum resistance thermometer gave indications about 1.2°C. lower than those of the nitrogen thermometer. For the actual error of the platinum thermometer at low temperatures reference should be made to its comparison with the hydrogen thermometer.

A comparison of the previously calibrated thermocouple with the corrected indications of the platinum resistance thermometer was obtained by measuring the freezing point of ammonia with each instrument. The freezing points so determined agreed within

[35] Bur. St. Circ., **35,** 1919.

[36] Henning, Ann. der Phys., **40,** p. 635, 1913.

TABLE XV

**Comparison of Platinum Resistance Thermometer with Nitrogen Thermometer**

| Date | *Pressure* | | *Resistance ohms* | $t_{N_2}$ °C | $t_{pt}$ °C | $t_{N_2}-t_{pt}$ °C |
|---|---|---|---|---|---|---|
| | $P_0$ *mm.* | $P_t$ *mm.* | | | | |
| 11/21/21 | 728.07 | 648.37 | 22.5149 | − 29.84 | − 29.76 | −0.08 |
| 11/21/21 | 728.07 | 483.47 | 16.1545 | − 91.56 | − 91.56 | 0 |
| 11/21/21 | 728.07 | 420.47 | 13.6843 | −115.13 | −115.27 | +0.14 |
| 11/21/21 | 728.07 | 392.97 | 12.5962 | −125.43 | −125.68 | +0.25 |
| 11/21/21 | 728.07 | 238.20 | 6.3740 | −183.33 | −184.49 | +1.16 |
| 12/ 9/21 | 728.11 | 649.37 | 22.5466 | − 29.48 | − 29.45 | −0.03 |
| 12/ 9/21 | 728.11 | 556.36 | 18.9815 | − 64.29 | − 64.23 | −0.06 |
| 12/ 9/21 | 728.11 | 456.19 | 15.0845 | −101.78 | −101.83 | +0.05 |
| 12/ 9/21 | 728.11 | 371.01 | 11.7230 | −133.65 | −133.95 | +0.30 |
| 12/20/21 | 728.06 | 238.10 | 6.3699 | −183.37 | −184.53 | +1.16 |
| 12/21/21 | 728.06 | 237.69 | 6.3522 | −183.52 | −184.70 | +1.18 |

0.01°C. This agreement is especially satisfactory in that at this temperature (−77.8) the platinum thermometer reads higher than the gas thermometer, a fact not to be expected from the work of previous investigators. The freezing point of ammonia thus determined will be given in conjunction with the other fixed points.

### *Boiling Points of Carbon Dioxide and Oxygen*
### *(Preliminary)*

The boiling points of carbon dioxide and oxygen were measured in a vapor pressure manometer (p. 301) with the platinum resistance thermometer. The boiling point of $CO_2$ at 720.2 mm. was found to be −79.21°C. on the scale of the nitrogen thermometer. The temperature-vapor pressure equation of Henning[37] for $CO_2$ gives −79.18°C. at this pressure. The boiling point of oxygen, corrected to normal pressure by the equation of Cath,[38] was found to be −183.55°C., while the temperature of free boiling oxygen at normal pressure was found by direct immersion of the resistance thermometer in the liquid to be −183.46°C. on the nitrogen scale.

[37] Henning, Ann. der Phys., **43**, p. 287, 1914.

$$\text{For } CO_2 : T = \frac{194.584}{1-0.14428 \log (p/760)}$$

[38] Cath. Leiden Comm., **152d**, 1918.

$$\text{For } O_2 : \log p = -\frac{419.3}{T} + 5.2365 - 0.00648T$$

In view of the fact that the best previous determinations of the oxygen point all gave values between −182.90°C. and −183.00° C. our value appeared much too low. Thus the nitrogen thermometer agreed within 0.03°C. with the hydrogen thermometer of Henning, at least down to −80°C.; but at lower temperatures deviated in the direction of values which were too low. In order to determine whether this deviation was really due to a thermodynamic property of the gas, as is commonly supposed, the effect of varying the initial pressure of the gas was tried. The result of this experiment has already been given (p. 253), leading to the conclusion that the deviation was independent of the initial pressure between 640 mm. and 440 mm. No proof is thus afforded that the pressure of the nitrogen is not a linear function of the temperature at constant volume at −183°C. A deviation of the nitrogen scale from that of hydrogen at low temperatures is established, however, and the thermometer bulb was filled with hydrogen in order to obtain a direct comparison of the two scales over the whole range of the experiments.

### *E. Measurements with the Hydrogen Thermometer*

The thermometer was loaded with hydrogen in the manner previously described for nitrogen. Owing to diffusion no attempt was made to determine the pressure coefficient experimentally, the value being obtained by calculation from the equation of state. This value at the initial pressure of 763.2 mm. is 0.0036624. Henning gives 0.0036617 for the same pressure, whereas the value calculated for 1100 mm. or 0.0036629, is in almost exact agreement with the value 0.0036628 obtained by Onnes. If the temperature of the bulb is never raised above that of the room, no serious difficulty will be caused by diffusion. Over a period of twenty days the ice-point pressure decreased at a rate of only 0.013 mm. per twenty-four hours.

### *Platinum Resistance Thermometer Comparison*

A comparison of the platinum resistance thermometer with the hydrogen thermometer was now made. The cryostat previously described was available for measurements down to −145°C., at which point the pentane bath becomes viscous. Comparisons at a lower temperature were carried out directly in liquid oxygen. Electrolytic oxygen was dried by phosphorus pentoxide *P* (Fig. 13), and forced at a pressure of about twenty pounds per square inch through the copper coil *C* immersed in liquid air. A continuous stream of oxygen was thus formed which could be collected in the Dewar tube *D* and transferred to the vessel containing the thermometers.

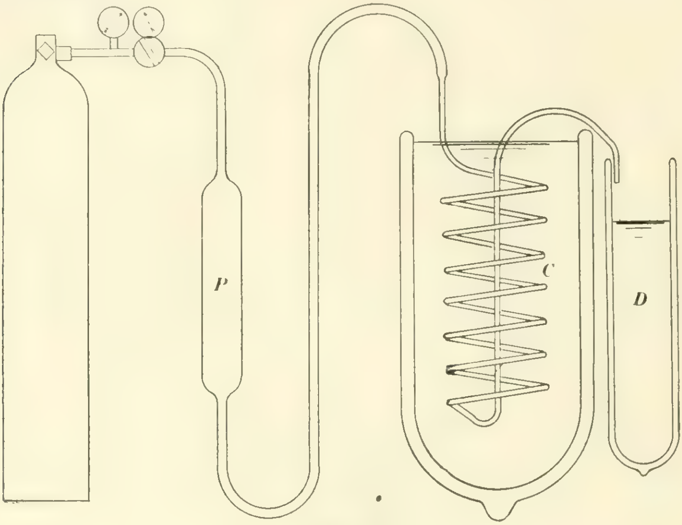

**Fig. 13**

The results of the comparison are given in Table XVI. Curve *A* of Fig. 14 exhibits the deviations of the temperatures derived from the platinum resistance thermometer and the Callendar formula from the hydrogen scale. Curve *B* gives the deviations of the platinum thermometer from the nitrogen scale based on Table XV and plotted against hydrogen temperatures. The deviations from the hydrogen scale are considerably larger at low temperatures than those found in the case of nitrogen, but are still smaller than the deviations found by Henning. Moreover, between 0°C. and −83°C. the resistance thermometer reads too high, whereas Henning found no deviation between 0° and −40° and below the latter temperature the resistance thermometer indicated increasingly too low temperatures.

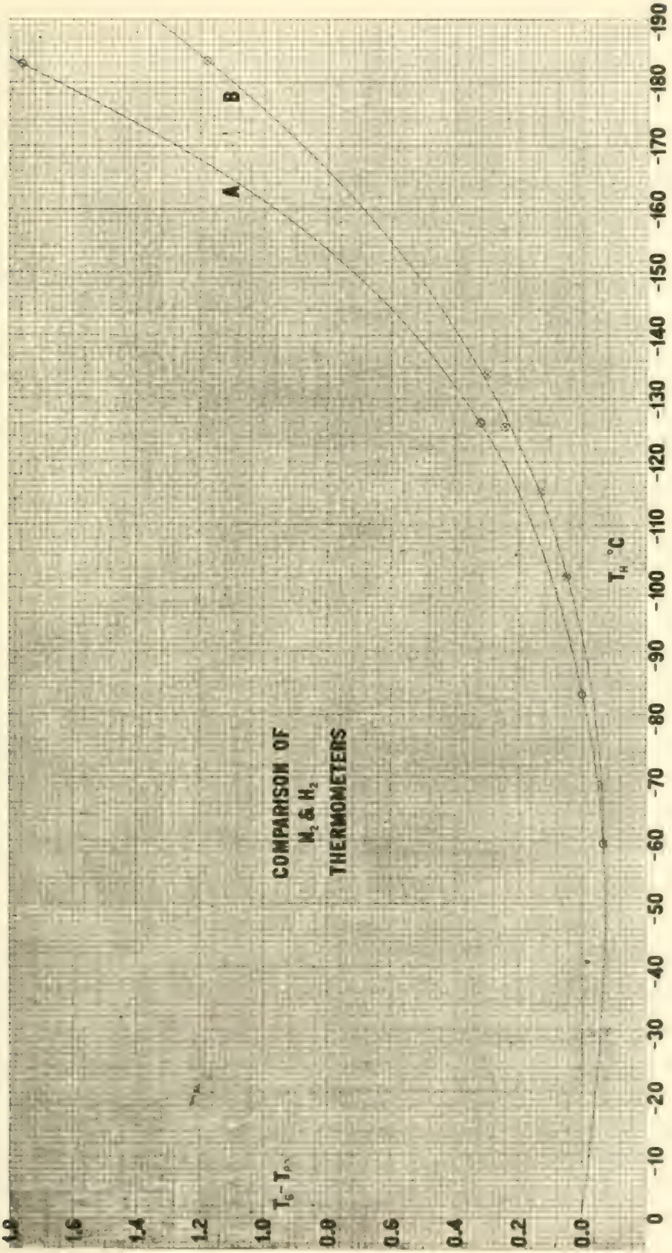
COMPARISON OF
$N_2$ & $H_2$
THERMOMETERS
A
B
$T_G - T_H$
$T_H$ °C
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8

Fig. 14

The deviations of a platinum resistance thermometer must be, to a certain extent, dependent upon the particular instrument employed, since they are certainly in part caused by strains in the wire, due to unequal contraction on its support. Thus the results of Henning and the above measurements clearly indicate a large deviation of the platinum resistance thermometer at low temperatures of the approximate magnitude given, and, furthermore, that the deviations of any particular instrument must be independently investigated. A type of support which would not set up strains in the wire under large temperature changes would be a great advantage, and the deviations of an instrument so constructed might possibly possess a considerable degree of generality.

**TABLE XVI**

**Comparison of Platinum Resistance Thermometer with Hydrogen Thermometer**

| | *Pressure* | | | | | |
|---|---|---|---|---|---|---|
| *Date* | $P_0$ *mm.* | $P_t$ *mm.* | *Resistance ohms* | $t_{H_2}$ °C | $t_{pt}$ °C | $t_{H_2}-t_{pt}$ °C |
| 4/ 6/22 | 763.20 | 596.93 | 19.4758 | − 59.48 | − 59.41 | −0.07 |
| 4/ 6/22 | 763.20 | 530.89 | 17.0288 | − 83.11 | − 83.11 | 0 |
| 4/ 6/22 | 763.20 | 410.67 | 12.5120 | −126.12 | −126.44 | +0.32 |
| 3/20/22 | 763.23 | 251.67 | 6.348 | −183.01 | −184.85 | +1.84 |
| 3/20/22 | 763.23 | 251.77 | 6.352 | −182.97 | −184.81 | +1.84 |
| 3/20/22 | 763.23 | 251.80 | 6.354 | −182.96 | −184.79 | +1.83 |
| 3/30/22 | 763.17 | 252.82 | 6.386 | −182.60 | −184.36 | +1.76 |
| 3/30/22 | 763.16 | 252.57 | 6.377 | −182.68 | −184.45 | +1.77 |

### *Comparison of Nitrogen and Hydrogen Thermometers*

The platinum resistance thermometer having been carefully compared with the nitrogen and hydrogen thermometers under exactly similar conditions, we are now in a position to find the deviations of the nitrogen scale from that of hydrogen. These can be found directly from Fig. 14 and are, for convenience, tabulated in Table XVII. As had been expected from the previous measurements with the nitrogen thermometer, there is no difference in the indications of the two instruments down to −70°C. At −80° the difference amounts to 0.02° and increases more and more rapidly with lowering temperatures until at the oxygen point it becomes 0.60°. Furnished with these deviations we can now correct all temperatures measured with the thermocouple to the scale of the hydrogen thermometer.

The deviations of the nitrogen thermometer from the hydrogen scale will be ascribed, by those familiar with gas thermometry, to a property of the gas itself; although there is difficulty in explaining the difference of 0.60° at −183° in view of the fact that the Berthelot correction at this temperature and initial pressure would be somewhat less than 0.4°. The usual interpretation is rejected, however, in view of the facts presented. Within the limits of experimental measurements it has been found that the isometrics of gases sufficiently removed from their condensation points are straight lines. Direct experimental evidence, moreover, of a thermodynamic correction could not be found, in that the indications of the nitrogen thermometer at −183°C. were independent of a large change in the initial pressure. Other possible causes of the divergence in the two gas thermometers are evident since condensible impurities in the gas, association, and adsorption would all cause a similar effect. Inasmuch as the gas was carefully prepared and passed through liquid air before being admitted to the bulb, the possibility of condensible impurities in sufficient amount to seriously affect the results must be ruled out. At −183° and a pressure of a third of an atmosphere the gas is still far enough from its condensation point to make it improbable that association of the molecules could more than partly account

**TABLE XVII**

**Deviations of the Nitrogen Thermometer from the Hydrogen Scale**

| $t_{H_2}$ °C | $t_{H_2}-t_{N_2}$ °C | $t_{H_2}$ °C | $t_{H_2}-t_{N_2}$ °C |
|---|---|---|---|
| − 70 | +0.01 | −140 | +0.14 |
| − 80 | +0.02 | −150 | +0.19 |
| − 90 | +0.04 | −160 | +0.28 |
| −100 | +0.05 | −170 | +0.40 |
| −110 | +0.06 | −180 | +0.55 |
| −120 | +0.08 | −183 | +0.60 |
| −130 | +0.10 | | |

for the deviations. That adsorption takes place at low temperatures is well known, and it is of interest to form an estimate of how much adsorption would be necessary to explain the observed deviation. The area of the bulb is approximately 120 sq. cm. and taking the area occupied by one molecule to be $(3\times10^{-8})^2$ it is found that there would be $13.3\times10^{16}$ molecules in one adsorbed layer. This corresponds to $6.14\times10^{-6}$ grams per layer. If the pressure is decreased by $\Delta p$ due to adsorption, the total fraction of gas adsorbed is $\Delta p/p$. The total number of grams adsorbed to produce a lowering of the pressure by $\Delta p$ will then be $\frac{\Delta p}{RT}.\, v$ or $31.5\,\frac{\Delta p}{T}$. Hence the number of layers necessary to account for the effect is $\frac{31.5}{6.14\times10^{-6}}.\frac{\Delta p}{T} = 5.13\times10^{6}\,\frac{\Delta p}{T}$, where $\Delta p$ is expressed in atmospheres.

TABLE XVIII
Adsorption of Nitrogen

$$L = 5.13\times10^{6}\ \frac{\Delta p}{T}$$

| *$T_H$ Degrees Kelvin* | *$T_H - T_N$* | *$\Delta P$ mm.* | *Number of Layers* |
|---|---|---|---|
| 203 | .01 | .03 | 1 |
| 193 | .02 | .05 | 2 |
| 183 | .04 | .11 | 4 |
| 173 | .05 | .13 | 5 |
| 163 | .06 | .16 | 7 |
| 153 | .08 | .21 | 9 |
| 143 | .10 | .27 | 13 |
| 133 | .14 | .37 | 19 |
| 123 | .19 | .51 | 28 |
| 113 | .28 | .75 | 45 |
| 103 | .40 | 1.07 | 70 |
| 93 | .55 | 1.47 | 106 |
| 90 | .61 | 1.63 | 122 |

In Table XVIII are given the number of layers of nitrogen adsorbed necessary to account for the deviation of the nitrogen from the hydrogen thermometer on the assumption that adsorption is negligible in the latter case. These must be regarded as maximum values since the area of the bulb surface calculated from its dimensions is a lower limit. The effective area for adsorption may be several times as great owing to the unevenness of the surface with respect to molecular dimensions. Thus it would not be unreasonable to suppose that due to this circumstance the deviation at −183°C. might be accounted for by adsorption to a depth of only thirty or forty layers. Whether adsorption of nitrogen and other gases on quartz at low temperatures takes place to such an extent is of course an open question. No reliable data are at hand. Langmuir,[39] however, found that glass and mica strongly adsorbed nitrogen at liquid air temperatures at only 0.1 mm. pressure; while the adsorption of hydrogen he found to be very much less. It thus appears that the deviation of the nitrogen thermometer from the hydrogen scale at low temperatures finds a ready explanation in the combined effects of adsorption and association.* Of these two the former would appear to be the larger. In the case of the hydrogen thermometer the indications are that any error due to adsorption at liquid air temperatures is extremely small.

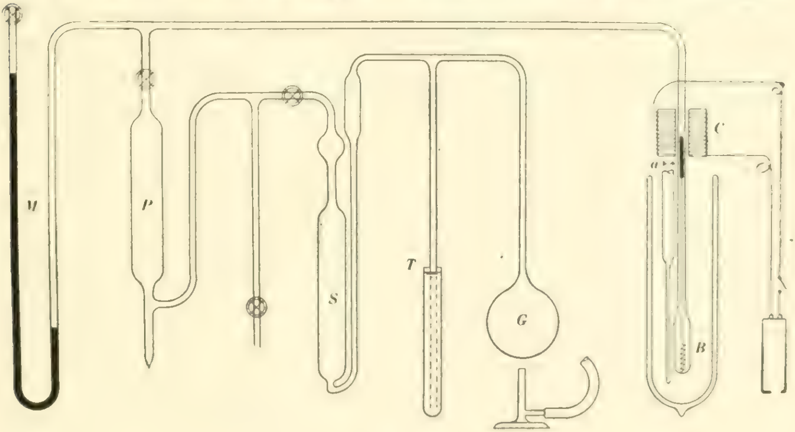

Fig. 15

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[39] Langmuir, J. Am. Ch. Soc. 39, 1917.

*That variation of the inital pressure is without effect is due to adsorption being independent of the pressure above a certain point. Thus, on metals the amount of gas adsorbed remains constant above a pressure of 300 mm. according to Taylor and Burns, J. Am. Ch. Soc., **43**, p. 1273, 1921.

### *The Boiling Point of Oxygen*

A determination of the boiling point of oxygen based on the nitrogen thermometer has already been noted. It is now possible to transfer this to the hydrogen (thermodynamic) scale. The determination was carried out by means of the apparatus shown in Fig. 15. The oxygen was prepared in *G* by the decomposition of potassium permanganate. It was passed through sodium hydroxide (20 per cent) *S*, and phosphorus pentoxide *P* and condensed in the bulb *B* (ca. 10 c.c.) surrounded by liquid air. The tube *T*, dipping into mercury, acted as a valve, limiting the pressure to about ninety centimeters of mercury. The liquid in *B* could be electromagnetically stirred by means of the iron stirrer *a* and the coils *C*. The vapor pressure of the liquid was read directly on the manometer *M* and its temperature found with the platinum resistance thermometer. The apparatus was exhausted and swept out several times with oxygen before proceeding with the measurements. To test the purity of the oxygen about one-half of the liquid in *B* was allowed to evaporate and the vapor pressure of the remainder determined, being found to give the same value as before.

The normal boiling point of oxygen thus found is 182.94°C., the details of the measurements being given in Table XIX. The agreement of our value with the latest value of Onnes,[40] −182.93° C. (or −182.97° uncorrected), is excellent.

**TABLE XIX**
**Oxygen Boiling Point**

| *Date* | $t_{pt.}$ °C | $t_{H_2}$ °C | *Vapor Pressure mm.* | $\frac{\Delta p^i}{\Delta t}$ *mm./deg.* | *N.B.P.* °C |
|---|---|---|---|---|---|
| 12/23/21 | −184.41 | −182.64 | 784.4 | 81.8 | −182.94 |
| 12/23/21 | −184.36 | −182.60 | 787.9 | 82.3 | −182.94 |

### *The Boiling Point of Carbon Dioxide*

The boiling point of carbon dioxide was determined in the same vapor pressure manometer that was used for oxygen. The gas was prepared by the decomposition of sodium bicarbonate and dried with phosphorus pentoxide. The bulb (Fig. 15) was immersed in a freezing mixture of carbon dioxide snow and ether, whereupon the carbon dioxide condensed in the form of perfectly clear ice. The vapor pressure was found independent of the amount of substance, thus attesting to its purity. Observations were taken at a pressure of 720.2 mm. and the boiling point at this pressure was found to be −79.19°C. on the hydrogen scale. This is in excellent agreement with the value of −79.18°C. given by the formula of Henning.[37] The details of the measurements follow:

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[40] Cath., Leiden Comm., **152d**, see Note 1, p. 48.

**Boiling Point of Carbon Dioxide**

| *Date* | $t_{pt}$ | $t_{H_2}$ | *Vapor Pressure mm.* | $\frac{\Delta p}{\Delta t}$ *mm./deg.* | *N.B.P. °C* |
|---|---|---|---|---|---|
| 1/12/22 | −79.17 | −79.17 | 720.2 | 60.3 | −78.53 |

## Part II

## *Freezing Points of Certain Organic Liquids and of Mercury and Ammonia*

Certain freezing points have been measured in the range from 0°C. to −123°C. in order to establish fixed points for thermometric comparison. The temperatures were obtained with the multiple copper-constantan thermocouple described in Part I, p. 290, which had been repeatedly calibrated directly against the nitrogen constant volume thermometer. A direct comparison of the nitrogen and hydrogen thermometers enables us to give the freezing points directly on the constant volume hydrogen, or thermodynamic, scale.

### *The Method*

The electrical circuit has been described as noted above. The liquid whose freezing point is to be determined is contained in the double-walled vessel *A* (Fig. 16A), 2 cm. in diameter and 13 cm. long. The space between the walls of this vessel is connected to the vacuum pump and can be exhausted to any desired degree, thus controlling the rate of cooling. Cooling is obtained by liquid air in the outer Dewar tube *B*. The liquid is stirred by a stream of dry air entering through the fine glass tube *S*, further serving to keep the space above the liquid free of moisture. It was found that the freezing points were independent of the rate of stirring between wide limits, but that some stirring was necessary to give concordant results. In determining the freezing points of organic liquids a thermocouple possesses a marked advantage in that it records the temperature at a definite point. The thermal conductivity of the two phase mixtures is so low that it is practically impossible to secure uniformity of temperature throughout a large mass of the liquid as the freezing point is approached and an instrument of considerable bulk will consequently register an average temperature which may not be the true freezing point, at least in those cases where ice forms first at the bottom of the tube and builds upward.

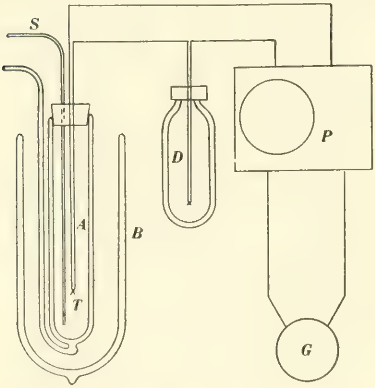

**Fig. 16a**

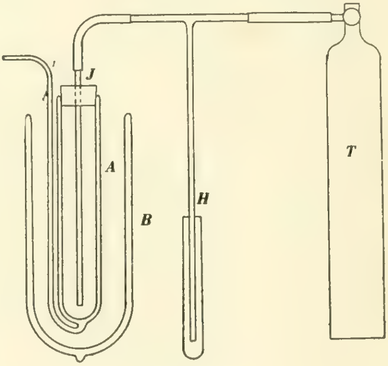

**Fig. 16b**

In determining the freezing points of liquids which are gaseous at ordinary temperatures, such as methyl chloride and ammonia, the tube *A* was first well cooled, whereupon the gas from the supply *T* (Fig. 16B) was admitted through the glass tube *J*. It then rapidly liquefied under the slight excess of pressure. The tube *H*, dipping into mercury, prevented the pressure from becoming more than a few centimeters of mercury above atmospheric.

### *The Results*

The individual determinations are given in Tables XX-XXX. The methods of purification, starting with the best C. P. chemicals obtainable, are also given.* Column 5 gives the average cooling rate during the five minutes preceding freezing. The freezing points of mercury, ammonia, and methyl chloride are easily reproducible and constitute the most satisfactory fixed points. The ammonia point was likewise measured with the platinum resistance thermometer, the two methods agreeing within 0.01°C. In some measurements a silvered tube was used in place of the clear glass Dewar tube *A* without affecting the results. A considerable variation in the dimensions of the freezing point tube was likewise without effect on the constancy of the freezing points. The freezing point found for an organic liquid depends somewhat upon the method employed and the thoroughness of the purification. The results here given will be found reproducible provided the general method of procedure is followed.

In Table XXXI the various fixed points are summarized, including the determinations of the boiling points of carbon dioxide and oxygen recorded in Part I. For the sake of comparison the results of other investigators are also given.

TABLE XX

**Carbon Tetrachloride** †

$CCl_4$

| *Date* | *E.M.F.* $10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point* °C |
|---|---|---|---|---|
| 5/25/21 | 4957 | 8 | 0.67 | −22.85 |
| 5/25/21 | 4962 | 9 | 0.73 | −22.86 |
| 6/ 6/21 | 4960 | 7 | 0.77 | −22.86 |
| 6/ 6/21 | 4959 | 7 | 1.03 | −22.86 |
| 6/ 6/21 | 4965 | 5 | 2.14 | −22.89 |
| 6/ 6/21 | 4966 | 5 | 2.44 | −22.89 |

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* The chemicals were kindly prepared by Mr. R. S. Taylor of the Research Laboratory of Physical Chemistry.

† *Purification.* Warm with alcohol and caustic potash to remove $CS_2$ and $SCl_2$. Remove alcohol by shaking with water. Remove water over caustic potash and finally over sodium, lastly distill over paraffin, whereby the small quantity of perchlorethane is held back.

### TABLE XXI

**Mercury***
**Hg.**

| *Date* | *E.M.F.* $10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point °C* |
|---|---|---|---|---|
| 6/24/21 | 8264 | Indefinite | 1.29 | −38.90 |
| 6/24/21 | 8264 | Indefinite | 1.57 | −38.90 |
| 8/30/21 † | 8262 | Indefinite | 1.51 | −38.89 |
| 8/30/21 † | 8264 | Indefinite | 0.98 | −38.90 |

* *Purification.* Agitate with dilute nitric acid and distill several times.
† Silvered tube.

### TABLE XXII

**Chlorbenzene***
**$C_6H_5Cl$**

| *Date* | *E.M.F.* $\times 10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point °C* |
|---|---|---|---|---|
| 5/16/21 | 9590 | 31 | 2.40 | −45.58 |
| 5/17/21 | 9584 | 30 | 1.79 | −45.53 |
| 6/ 7/21 | 9595 | 10 | 3.17 | −45.62 |
| 6/ 7/21 † | 9590 | 12 | 3.65 | −45.58 |
| 6/ 7/21 | 9590 | 50 | 2.89 | −45.58 |
| 6/ 9/21 † | 9590 | 10 | 1.04 | −45.58 |
| 8/26/21 † | 9589 | 5 | 2.54 | −45.57 |

* *Purification.* Wash with water and dilute $NaOH$. Dry over $CaCl_2$ and distill with fractionating column three or four times. Dry over metallic sodium and again distill.

† Silvered tube.

### TABLE XXIII

**Chloroform***
**$CHCl_3$**

| *Date* | *E.M.F.* $10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point °C* |
|---|---|---|---|---|
| 5/20/21 | 13141 | 2 | 1.34 | −64.15 |
| 5/20/21 | 13160 | 8 | 0.05 | −64.24 |
| 5/20/21 | 13147 | 12 | 2.11 | −64.17 |
| 5/20/21 | 13134 | 3 | 0.82 | −64.11 |
| 6/ 8/21 | 13151 | 2 | 1.67 | −64.20 |
| 6/ 8/21 | 13160 | 2 | 2.13 | −64.24 |
| 6/ 8/21 | 13149 | 3 | 1.03 | −64.18 |
| 6/ 9/21 | 13157 | 4 | 1.04 | −64.23 |
| 6/ 9/21 | 13154 | 8 | 1.48 | −64.21 |
| 6/ 9/21 | 13154 | 3 | 1.56 | −64.21 |

* *Purification.* Agitate with pure concentrated $H_2SO_4$ until the acid is no longer colored. Next wash with $Na_2CO_3$ and then with alkaline permanganate. Wash with distilled water, dry over sodium and distill.

### TABLE XXIV

Ammonia*

$NH_3$

| *Date* | *E.M.F.* $10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point* °*C* |
|---|---|---|---|---|
| 6/20/21 | 15634 | 28 | 0.81 | −77.80 |
| 6/20/21 | 15634 | 25 | 0.80 | −77.80 |
| 8/25/21 † | 15635 | 6 | 1.28 | −77.80 |
| 8/25/21 † | 15634 | 33 | 1.05 | −77.80 |

* *Purification.* Dry with sodium.

† Silvered tube.

### TABLE XXV

Toluene*

$C_6H_5CH_3$

| *Date* | *E.M.F.* $10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point* °*C* |
|---|---|---|---|---|
| 5/13/21 | 18729 | 5 | 0.76 | −95.71 |
| 5/16/21 | 18730 | 5 | 1.28 | −95.71 |
| 5/31/21 | 18730 | 4 | 0.79 | −95.71 |
| 6/ 4/21 | 18723 | 4 | 2.33 | −95.67 |
| 6/ 9/21 † | 18726 | 4 | 1.58 | −95.68 |
| 6/22/21 | 18734 | 13 | 0.71 | −95.73 |
| 6/22/21 | 18730 | 10 | 1.21 | −95.71 |
| 7/19/21 | 18728 | 6 | 1.58 | −95.70 |
| 7/19/21 | 18726 | 11 | 1.27 | −95.69 |
| 8/31/21 † | 18727 | 12 | 0.57 | −95.69 |

* *Purification.* Free of phenols by *NaOH*. Shake with concentrated $H_2SO_4$ until acid is no longer colored. Agitate with mercury until it ceases to pollute a clean *Hg* surface. Wash and distill several times. Dry with $CaCl_2$ and sodium.

† Silvered tube.

### TABLE XXVI

Methyl Chloride*

$CH_3Cl$

| *Date* | *E.M.F.* $10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point* °*C* |
|---|---|---|---|---|
| 6/23/21 | 19172 | 5 | 1.28 | −98.39 |
| 6/23/21 | 19172 | 11 | 0.84 | −98.39 |

* Taken from the top of a tank of the commercially pure gas.

### TABLE XXVII

**Methyl Alcohol***

$CH_3OH$

| Date | *E.M.F.* $10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point* °*C* |
|---|---|---|---|---|
| 6/17/21 | 19197 | 6 | 1.01 | −98.54 |
| 6/17/21 | 19194 | 8 | 1.03 | −98.53 |

* *Purification.* Treat with iodine and then with slight excess *NaOH*. Reflux over fresh quicklime and finally dry with metallic calcium. Keep moist air away.

### TABLE XXVIII

**Carbon Disulphide***

$CS_2$

| Date | *E.M.F.* $10^{-6}$ *Volts* | *Time Minutes* | *Cooling Rate Deg./Min.* | *Freezing Point* °*C* |
|---|---|---|---|---|
| 6/16/21 | 21484 | 2 | 2.54 | −112.96 |
| 6/16/21 | 21486 | 3 | 2.49 | −112.97 |
| 6/16/21 | 21483 | 4 | 0.62 | −112.95 |
| 6/17/21 | 21488 | 3 | 0.40 | −112.97 |
| 8/27/21 † | 21491 | 8 | 1.10 | −113.00 |
| 8/27/21 † | 21488 | 5 | 0.68 | −112.98 |

* *Purification.* Digest with finely divided copper powder or with mercury over a water bath. Distill repeatedly. Dry with $CaCl_2$ and *Na*.

† Silvered tube.

### TABLE XXIX

**Ether***

$(C_2H_5)_2O$

| Date | *First Modification* † | | *Cooling Rate Deg./Min.* | *Freezing Point* °*C* |
|---|---|---|---|---|
| | *E.M.F.* $\times 10^{-6}$ *Volts* | *Time Minutes* | | |
| 6/13/21 | 23052 | 7 | 1.47 | −123.40 |
| 6/15/21 | 23052 | 27 | 1.58 | −123.40 |
| 6/15/21 | 23046 | 5 | 1.60 | −123.36 |
| 6/15/21 | 23054 | 28 | 1.76 | −123.42 |
| 6/16/21 | 23053 | 15 | 1.33 | −123.41 |

* *Purification.* Shake with conc. $H_2SO_4$. Then leave with 200 c.c. of a sat. sol. of $KMnO_4$ containing 20 gms. of *NaOH* per liter. After 24 hours decant and repeat. Wash with water. Let stand over $H_2SO_4$ shortly. Dry over $CaCl_2$, then distill and dry over sodium.

† The first modification occurred more often and gave the better point although the second modification is considered the more stable (see Table XXX).

| Date | *Second Modification* | | Cooling Rate Deg./Min. | Freezing Point °C |
|---|---|---|---|---|
| | E.M.F. $\times 10^{-6}$ *Volts* | *Time Minutes* | | |
| 6/13/21 | 21890 | 20 | — | −115.6 |
| 6/13/21 | 21921 | 39 | 0.37 | −115.7 |
| 6/15/21 | 21990 | 17 | 1.60 | −116.3 |

## TABLE XXX

### Detail of Ether Run Showing Both Modifications

*6/15/21*

| *Time in Minutes* | *Reading in Microvolts* | *Time in Minutes* | *Reading in Microvolts* | *Time in Minutes* | *Reading in Microvolts* | *Time in Minutes* | *Reading in Microvolts* |
|---|---|---|---|---|---|---|---|
| 0 | 22395 | 8 | 23036 * | 16 | 21988 † | 24 | 21991 † |
| 1 | 22650 | 9 | 23050 * | 17 | 21991 † | 25 | 21993 † |
| 2 | 22859 | 10 | 21996 | 18 | 21990 † | 26 | 21994 † |
| 3 | 23069 | 11 | 21987 † | 19 | 21990 † | 27 | 21992 † |
| 4 | 23243 * | 12 | 21987 † | 20 | 21990 † | 28 | 21991 † |
| 5 | 23054 * | 13 | 21990 † | 21 | 21990 † | 29 | 22010 |
| 6 | 23039 * | 14 | 21991 † | 22 | 21991 † | 30 | 22064 |
| 7 | 23049 * | 15 | 21991 † | 23 | 21991 † | 31 | 22164 |

* One. † Two.

## TABLE XXXI

Fixed Points Between O°C and −*183*°C Absolute Centigrade Temperatures

| *Substances* | *K, T, & Y* | *Henning*[37] | *Onnes*[39] | *Timmerman's*[40] | *Brill*[41] | *Wilhelm*[42] | *Travers,*[29] *Senter and Jacquerod* |
|---|---|---|---|---|---|---|---|
| Carbon Tetrachloride, $CCl_4$ | − 22.87 | | | − 22.90 | | | |
| Mercury | − 38.90 | − 38.89 | | | | −38.87 | |
| Chlorbenzene, $C_6H_5Cl$ | − 45.58 | − 45.54 | | − 45.2 | | | |
| Chloroform, $CHCl_3$ | − 64.19 | − 63.7 | | − 63.5 | | | |
| Ammonia, $NH_3$ | − 77.80 | | | | 77.7 | | |
| Carbon Dioxide, $CO_2$(N.B.P.) | − 78.53 | − 78.52 | | | | | |
| Toluene, $C_6H_5CH_3$ | − 95.70 | | | − 95.1 | | | |
| Methyl Chloride, $CH_3Cl$ | − 98.39 | | | | | | |
| Methyl Alcohol, $CH_3OH$ | − 98.54* | | | − 97.1 | | | |
| Carbon Disulphide, $CS_2$ | −112.97† | −112.0 | | −111.6 | | | |
| Ether (First Mod.) $(C_2H_5)_2O$ | −123.40 | −123.65 | | | | | |
| Ether (Second Mod.) | −115.9 | | | −116.3 | | | |
| Oxygen (N.B.P.) | −182.94 | −182.97 | −182.93 | | | | −182.93 |

[37] Ann. d. Phys., **43**, p. 282, 1914.

[39] Leiden Comm., **107a**, gives −182.99. (This has been corrected to −182.93 in L. C. 152d, p. 48, 1918.)

[40] C. r., **174**, p. 365, 1922.

[41] Ann. d. Phys., **21**, p. 170, 1906.

[42] Bull. Bur. St., **13**, p. 665, 1917.

[29] Phil. Trans. A, **200**, p. 105, 1903.

* Too hygroscopic for ready reproducibility.

† Reproducibility uncertain, owing perhaps, to small heat of fusion and difficulties of purification.

## Summary

A discussion of the constant volume gas thermometer and its errors has been given. Evidence has been cited leading to the conclusion that the pressure of a gas at constant volume is a linear function of the temperature, in which case the constant volume gas thermometer indicates directly on the thermodynamic scale. This conclusion has been supported by: first, an analysis of the isometrics of hydrogen calculated from the data of the Leiden laboratory; second, a recalculation of the boiling point of sulphur based on the data of the $H_2$, He and $N_2$ constant volume and the $N_2$ constant pressure gas thermometers (mean N. B. P. 444.56°), in which the value obtained from the constant volume nitrogen thermometer of Holborn and Henning, recalculated using the expansion coefficient given by the equation of state for nitrogen, was found to agree almost exactly, without correction to the thermodynamic scale, with the constant pressure nitrogen value of Eumorfopoulos corrected to the thermodynamic scale in accordance with the Keyes equation of state for nitrogen and with the value of Holborn and Henning derived from the constant volume helium and hydrogen thermometers; third, by direct experiment in which the indications of a constant volume nitrogen thermometer at $-183°$ were found independent of the initial pressure between 640 and 440 mm.

A constant volume hydrogen thermometer, capable of measuring temperatures with an accuracy of 0.01 per cent, has been described, together with a new form of cryostat in which low temperatures can be held constant to within 0.01°.

The copper-constantan thermocouple has been calibrated against the gas thermometer and the deviations of the platinum resistance thermometer from the absolute scale determined over the range from 0° to $-183°$. The platinum thermometer has been found to give too low a temperature at the boiling point of oxygen by about 1.6°; but the exact deviation depends upon the particular instrument employed.

A direct comparison of the nitrogen and hydrogen constant volume thermometers showed no divergence between the two scales down to $-70°$, while below this temperature the divergence

gradually increases until it amounts to 0.6° at the boiling point of oxygen. It has been shown that this divergence can be readily explained by the combined effects of association of the nitrogen and adsorption upon the walls of the quartz container.

The normal boiling point of carbon dioxide has been found to be −78.53°C. and that of oxygen −182.94°C. A detailed account has been given of a method of determining freezing points of various substances in the interval from −40° to −124° to serve as fixed points for thermometric comparison. These freezing points are:

| | |
|---|---|
| Carbon Tetrachloride, $CCl_4$ | − 22.87 |
| Mercury | − 38.90 |
| Chlorbenzene, $C_6H_5Cl$ | − 45.58 |
| Chloroform, $CHCl_3$ | − 64.19 |
| Ammonia, $NH_3$ | − 77.80 |
| Toluene, $C_6H_5CH_3$ | − 95.70 |
| Methyl Chloride, $CH_3Cl$ | − 98.39 |
| Methyl Alcohol, $CH_3OH$ | − 98.54 |
| Carbon Disulphide, $CS_2$ | −112.97 |
| Ether $(C_2H_5)_2O$, I. Mod. | −123.40 |
| Ether, II. Mod. | −115.9 |

Helium has been found to diffuse too readily through quartz at room temperatures to permit of its convenient use in a thermometer bulb of this material. Hydrogen likewise has been found to diffuse through quartz at ordinary temperatures, but so slowly as not to interfere with its use in quartz for low-temperature thermometry.

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# THE VAPOR PRESSURES, DENSITIES AND SOME DERIVED QUANTITIES FOR ETHER AT LOW TEMPERATURES

by

Robert S. Taylor and Leighton B. Smith

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 149]

# THE VAPOR PRESSURES, DENSITIES AND SOME DERIVED QUANTITIES FOR ETHER AT LOW TEMPERATURES

BY ROBERT S. TAYLOR AND LEIGHTON B. SMITH

Received August 1, 1922

## Introduction

This investigation was initiated to obtain better values for the saturation specific volumes of ethyl ether to be used in connection with the equation of state of the liquid phase. Incidental to the present investigation, further experience was gained in the operation and possibilities of the improved type of cryostat. In addition to the density measurements from +70° to —120°, vapor-pressure measurements were made in the temperature interval +20° to —60°.

Regnault[1] measured the vapor pressures and densities of ether above 0°. Later Young[2] obtained values over a range extending from slightly below 0° to the critical temperature. Seitz, Alterthum and Lechner[3] have published densities from the freezing point of ether to 0°. Mündel[4] measured a few vapor pressures at about the temperature of solid carbon dioxide, at one atmosphere (—78.5°). However, due to the fact that the pressures are very low below —70°, his results are only serviceable in giving the magnitude of the pressures.

In measuring the densities Young used a pycnometer of the U type such as is employed for liquids with low vapor pressures. Ether has an appreciable vapor pressure even at 0°, so that this is possibly not the best type of pycnometer. For the higher temperatures, Young floated ether on top of mercury in a jacketed manometer tube, determining the mass of ether by measuring the volume at a known temperature and density.

Seitz, Alterthum and Lechner measured the density from —110° to 0°. A borosilicate glass pycnometer was used of the same form as that employed in this investigation. The pycnometer had a long and rather large capillary to avoid the necessity of reloading to cover the temperature range. The temperatures, to the freezing point of mercury, were measured with a mercury thermometer, and lower temperatures were obtained by means of 2 Reichsanstalt calibrated pentane thermometers graduated to 0.1. To refrigerate the cryostat to —75° solid carbon dioxide was introduced into the bath from time to time, and for lower temperatures liquid air was dropped upon the surface of the petroleum-ether bath. The ether was purified by drying an imported "purest" ether over sodium.

[1] Regnault, *Mém. Acad.*, **26**, 339 (1862).

[2] Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374–443 (1910).

[3] Seitz, Alterthum and Lechner, *Ann. Physik*, **49**, 90 (1916).

[4] Mündel, *Z. physik. Chem.*, **85**, 435 (1913).

Keyes and Felsing[5] drew up a table of the most probable densities of ether from the work referred to above and from some measurements at 0° and −33° by Kenny and by Keyes and Felsing. They considered the densities above zero as measured by Young to be more accurate than those of Seitz, Alterthum and Lechner. Both sets of data seem to be about as accurate as the experimental procedure would permit.

## Apparatus and Method

For the density measurements the apparatus consisted of the cryostat, a quartz pycnometer, loading apparatus and the resistance thermometer. The same cryostat, loading apparatus and thermometer were used for the density measurements as were subsequently used with the addition of a special manometer for the vapor-pressure measurements.

**The Cryostat.**—The cryostat, shown in Fig. 1 consists of a large Pyrex Dewar tube L of about 6.3 cm. inside diameter. Inside this is a smaller Dewar tube S also of Pyrex glass, with a tube leading out from the bottom at D so that the amount of air between the walls of the inner tube could be varied at will. The inner tube contains a stirrer and heater H. Several designs of bimetallic regulators were tried, but they were not found to be as satisfactory as hand regulation. The outer Dewar tube was filled with liquid air or liquid ammonia as a cooling medium. Liquid air was found to be best for all temperatures, however, due to the convenience in handling. The inner tube was filled with bath liquid which would not freeze at the temperature at which it was used. Kerosene and gasolene were used for the higher temperatures, and from —40° to —120° petroleum ether or pentane was used.

The cryostat is of an improved design similar in principle to that first used by Cardoso[6] in his work on the critical constants of certain gases. If one has a good vacuum pump and regulates the degree of exhaustion very carefully until heat transfer between the bath and the cooling medium is small, good regulation can easily be obtained. It was found that, with a resistance thermometer sensitive to changes in temperature of 0.001° and with rapid stirring, the temperature could be maintained constant to within at least 0.01° by hand regulation. Pyrex glass was used in constructing the cryostat because of its greater thermal resistance as compared with soda glass The Dewar tubes were annealed before pumping. Thus far there has been no loss of Dewar tubes due to sudden or unequal cooling with the liquid air.

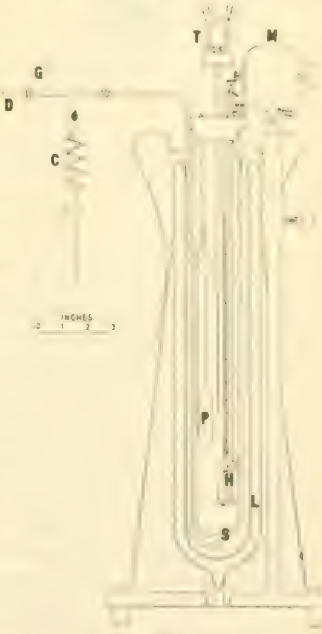

Fig. 1.

**The Pycnometer.** The quartz pycnometer shown at P in Fig. 1 had an approximate volume of 7.6 cc. The capillary was very uniform, having a volume of 0.0133 cc.

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[5] Keyes and Felsing, THIS JOURNAL, **41**, 589 (1919).

[6] Cardoso, *J. chim. phys.*, **15**, 317 (1915).

per cm. length. Above the capillary was a bulb of approximately 2.5 cc. capacity. The pycnometer was connected to the loading apparatus shown in Fig. 2 by means of a quartz-to-glass ground joint. The pycnometer was calibrated by filling with mercury, boiling to expel air and moisture, and weighing before and after determining the height in the capillary at various temperatures. This gave calibrations both of the bulbs and of the capillary, using the densities of mercury as determined by Callendar and Moss.

Since the volume of the capillary was small, the pycnometer had to be refilled for each temperature, and in some cases several fillings were made at the same temperature. It is difficult to mark graduations on quartz, and hence the height in the capillary was determined by means of a cathetometer and the bottom of the pycnometer was taken as the reference mark.

Quartz was used instead of glass in constructing the pycnometer because its coefficient of expansion is very small and the consequent corrections are small. Also, quartz is a pure substance and has a coefficient which does not vary with different samples as does that of glass. The dilatation of the pycnometer with pressure was obtained by filling with mercury and reading the volume under a pressure of 1 atmosphere. The pycnometer was then evacuated and the volume read again. The change in volume was found to be 0.000307 cc. per atmosphere for the volume used.

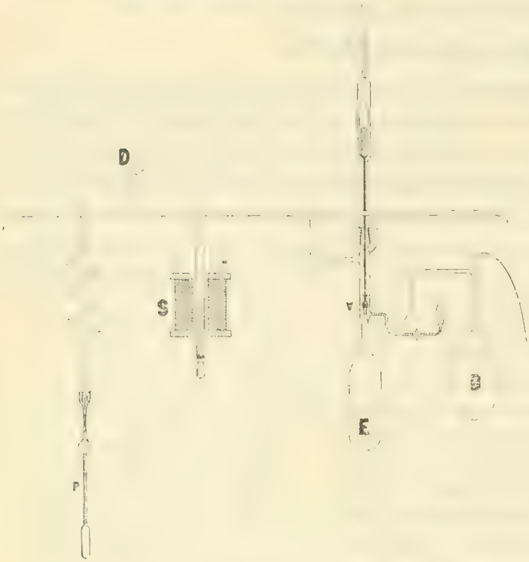

Fig. 2.

The expansion of quartz with rising temperature has been measured by a number of observers. Holborn and Henning[7] measured the mean coefficient of expansion over 250° intervals. Scheel and Chappuis[8] determined the mean coefficient between 15° and 57°, and 15° and 100°. They give an equation to represent their results. Harlow[9] measured the cubical expansion from 0° to 100°. Henning[10] observed the coefficient against glass from —191° to 16° and obtained the value $-4.64 \times 10^{-7}$ cm. per cm. length per degree C. This value is only approximate but it shows that, on the average, quartz expands in cooling to liquid air temperatures.

Scheel and Dorsey[11] determined the coefficient for 20° intervals from 0° to —160°. The expansion was measured by observing the shift of interference fringes. The temperature was measured by surrounding the quartz ring used with a calibrated resistance element. The temperatures were obtained by dipping the container to different depths in liquid air. Randall[12] made measurements above zero using the same principle.

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[7] Holborn and Henning, *Ann. Physik*, **10**, 446 (1903).

[8] Scheel and Chappuis, *Wiss. Abhand. Phys.-Tech. Reichsanst.*, **4**, 54 (1904).

[9] Harlow, *Proc. Phys. Soc. London*, **24**, 30 (1912).

[10] Henning, *Ann. Physik*, **22**, 606 (1907).

[11] Scheel and Dorsey, *Phys. Rev.*, **27**, 101 (1907).

[12] Randall, *ibid.*, **30**, 216 (1910).

The Scheel and Dorsey values seem to be the most consistent below zero and Randall's results are best above zero. It was found that the equation

$$\log (\alpha + 19) = \log 34.79 - \frac{50.789}{T} \tag{1}$$

best represented all values between −200° and +50° within the limits of experimental accuracy. This was integrated graphically for the mean coefficient from 0° to −25°,

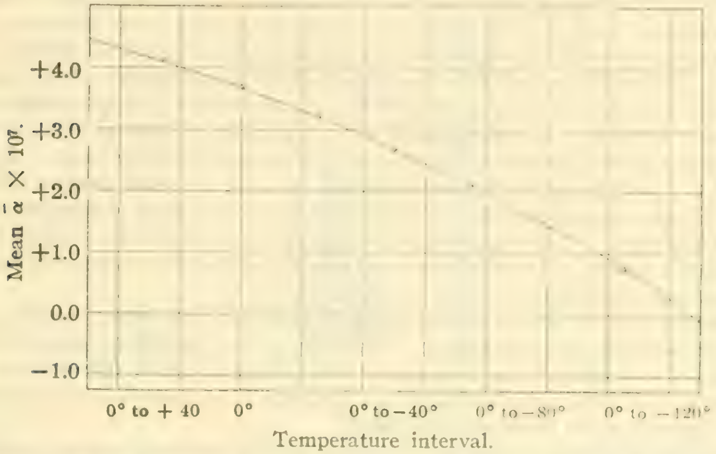

Fig. 3.—Mean coefficient of expansion of quartz plotted against temperature interval.

TABLE I

MEAN EXPANSION COEFFICIENTS OF QUARTZ

$\alpha \times 10^7$ calculated from the equation: $\log (\alpha + 19) = 1.5414 - \frac{50.789}{T}$

$$\bar{\alpha} = \frac{34.79 \int_{T_1}^{T_2} \epsilon^{-\frac{2.3b}{T}}}{T_2 - T_1} - 19$$

| $T°_{\text{abs.}}$ | $1/T \times 10^3$ | $\alpha$ observed $\times 10^7$ | $\alpha$ calc. $\times 10^7$ | Deviation | Interval of values ° C. | Temp. range 0° to ° C. | Mean $\bar{\alpha}$ $\times 10^7$ (calc.) |
|---|---|---|---|---|---|---|---|
| 113 | 8.85 | −6.65[a] | −6.63 | −0.02 | 20 | + 50 | +4.46 |
| 153 | 6.54 | −2.97[a] | −2.80 | −0.17 | 20 | + 25 | +4.11 |
| 183 | 5.46 | −0.64[a] | −0.63 | −0.01 | 20 | 0 | +3.67 |
| 193 | 5.18 | −0.468[a] | −0.02 | −0.45 | 20 | − 25 | +3.21 |
| 203 | 4.93 | +0.55[a] | +0.55 | 0.00 | 20 | − 50 | +2.68 |
| 233 | 4.29 | 2.110[a] | 2.06 | −0.05 | 20 | − 75 | +2.09 |
| 273 | 3.66 | 3.60[a] | 3.67 | +0.07 | 20 | −100 | +1.42 |
| 309 | 3.236 | 4.27[b] | 4.83 | +0.56 | 15– 56 | −125 | +0.76 |
| 322 | 3.106 | 4.23[c] | .... | .... | 16– 81 7 | −150 | −0.09 |
| 331 | 3.021 | 4.90[b] | .... | .... | 15–100 | −175 | −1.09 |
| 407 | 2.457 | 4.79[d] | .... | .... | 17–250 | .... | |

[a] Scheel and Dorsey.
[b] Scheel and Chappuis.
[c] Randall.
[d] Henning and Holborn.

and 0° to −50°, 0° to −75°, 0° to −100°, 0° to −125°, 0° to −150°, and 0° to −175°. These values were plotted with the temperatures and from the plot the mean coefficient of linear expansion from 0° to $t°$ could be read off. Table I contains observed and calculated values of mean coefficient, $\bar{\alpha}$. The plot is given in Fig. 3. From the values given, it is seen that the coefficient of expansion of quartz, in addition to being small, changes sign at about —80° and that at about —147° the pycnometer would have the same volume as at 0°. Evidently quartz is well suited for density work as regards its expansion behavior.

**Loading Apparatus.**—The loading apparatus shown in Fig. 2 was used to store the ether supply and keep it from contact with air, moisture and gaseous impurities.

The pycnometer P was connected by a quartz-to-glass ground joint as shown in the diagram. To load the pycnometer the ether was frozen and the parts of the apparatus previously open to the air evacuated through D by the mercury diffusion pump backed by a rotary oil pump. In testing for air in the apparatus, an iron rod with a glass bell attached was lifted by the solenoid S, whereupon ether could be distilled over, sufficient in amount to cover the bell when it was lowered. If there is any air present, the vapor phase will not collapse promptly under the slight hydrostatic head of liquid ether when the bell is dropped. The storage bulb E was finally warmed and the pycnometer cooled with liquid ammonia. The distillation was arrested again by cooling the storage bulb with liquid air, when sufficient ether had distilled over.

The pycnometer, after it was cooled with liquid air, was sealed from the storage apparatus with the oxygen-gas flame. It was found by trial that the amount of ether decomposed in sealing off the pycnometer was negligible, due to the very low vapor pressure at the temperature of liquid air. The amount of quartz lost by vaporization was also tested for and found to be negligible.

The same loading apparatus was employed to furnish the ether for the vapor-pressure measurements, being sealed to the vapor-pressure apparatus at L, Fig. 4, and then sealed off.

**The Thermometer.**—A platinum resistance thermometer T, Fig. 1, was used as already stated. This thermometer was calibrated at the ice, steam and naphthalene points to get the constants of the Callendar equation. The Callendar formula is not applicable at low temperatures as was shown by Henning.[13] The Henning corrections were used at first but later corrections obtained by actual comparison of the resistance thermometer with the hydrogen thermometer of Keyes, Townshend and Young[14] were used. The thermometer was calibrated by Townshend and Young down to the boiling point of liquid oxygen.

A purchased thermometer bridge, thermostated in this laboratory, was calibrated against U. S. Bureau of Standards' standardized resistances by means of a Carey-Foster bridge.

**The Manometer and Vapor-pressure Apparatus.**—A mercury manometer was used having a steel base and steel stopcocks as shown at A in Fig. 4. The arm, B, on the right had a sealed-in platinum needle which served as a fixed point for that arm. The contact was made by means of a buzzer amplifier system as shown. The interrupted low voltage direct current from I was amplified by the vacuum tube H and transmitted to the telephones T. Mercury was fed into the system to balance the pressure by means of the reservoir E, through the gas trap D and the final adjustment made with the small compressor C. The system was evacuated through V before loading with mercury or ether. The ether was stirred with the electromagnetic stirrer G operated by the metronome J.

The diameters of the 2 arms of the manometer were measured over the entire length of the tubes, before assembling, by weighing the mercury withdrawn from known lengths of column. This gave means of correcting for differences in capillary depression. The diameter of the tubes was large (1.3 cm.) in order to decrease the capillary depression. The same cathetometer was used as in the density work.

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[13] Henning, *Ann. Physik,* **40,** 345, 653 (1913).

[14] Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Tech.*, **1,** No. 4 (1922).

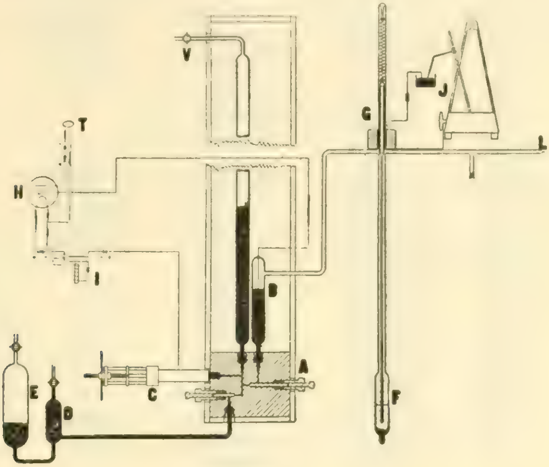

Fig. 4.

**Preparation of Material.**—The C. P. ether of trade was further purified by first shaking with conc. sulfuric acid until fresh portions produced no change of color. Then it was allowed to stand over a fresh quantity of acid overnight. After this treatment it was washed with water and poured into a saturated solution of potassium permanganate, containing 20 g. of sodium hydroxide per liter, to oxidize any aldehydes. After 24 hours the alkaline permanganate was removed and the treatment repeated. The ether was then washed, treated again with conc. sulfuric acid for a short time, washed, dried over calcium chloride and distilled. After drying over sodium ribbon it was again distilled. The ether was then allowed to stand over sodium ribbon for several weeks with additions of freshly prepared ribbon every few days. It was finally loaded into the bulb B of the storage apparatus (Fig. 2) from which it was distilled into the pycnometer or vapor-pressure apparatus through the 1-way valve V.

## Experimental Data

**Density of Liquid Ether.**—The densities observed and calculated are given in Table II. Since the density is almost a linear function of the

TABLE II

DENSITIES AND SPECIFIC VOLUMES OF ETHER

| No. | Temperature °C. | Density Calc. | Sp. vol. Calc. | Density Obs. | Values of other observers |
|---|---|---|---|---|---|
| 1 | −120 | 0.86195 | 1.16016 | 0.86195 | 0.8620[a] |
| 2 | −115 | 0.85699 | 1.16687 | ... | ... |
| 3 | −110 | 0.85200 | 1.17371 | 0.85192 | 0.8517[a] |
| 4 | −105 | 0.84699 | 1.18065 | | ... |
| 5 | −100 | 0.84196 | 1.18770 | | 0.8415[a] |
| 6 | −95 | 0.83690 | 1.19489 | | ... |
| 7 | −90 | 0.83182 | 1.20218 | ... | 0.8313[a] |
| 8 | −85 | 0.82672 | 1.20960 | ..... | ..... |

TABLE II (*Continued*)

| No. | Temperature °C. | Density Calc. | Sp. vol. Calc. | Density Obs. | Values of other observers |
|---|---|---|---|---|---|
| 9 | − 80 | 0.82159 | 1.21715 | 0.82141 | ..... |
| 10 | − 75 | 0.81643 | 1.22484 | 0.81640 | ..... |
| 11 | − 70 | 0.81126 | 1.23265 | 0.81114 | 0.8106[a] |
| 12 | − 65 | 0.80606 | 1.24060 | ..... | ..... |
| 13 | − 60 | 0.80084 | 1.24869 | ..... | ..... |
| 14 | − 55 | 0.79559 | 1.25693 | ..... | ..... |
| 15 | − 50 | 0.79032 | 1.26532 | 0.79032 | 0.7899[a] |
| 16 | − 45 | 0.78502 | 1.27385 | 0.78510 | ..... |
| 17 | − 40 | 0.77970 | 1.28254 | 0.77970 | ..... |
| 18 | − 35 | 0.77436 | 1.29139 | 0.77425 | ..... |
| 19 | − 30 | 0.76899 | 1.30041 | ..... | 0.7690[a] |
| 20 | − 25 | 0.76360 | 1.30959 | ..... | ..... |
| 21 | − 20 | 0.75819 | 1.31893 | ..... | ..... |
| 22 | − 15 | 0.75275 | 1.32846 | ..... | ..... |
| 23 | − 10 | 0.74729 | 1.33817 | ..... | 0.7474[a] |
| 24 | − 5 | 0.74180 | 1.34807 | 0.73629 | 0.73620[b] |
| 25 | 0 | 0.73629 | 1.35816 | | 0.73635[c] |
| 26 | + 5 | 0.73069 | 1.36857 | ..... | ..... |
| 27 | 10 | 0.72503 | 1.37925 | ..... | 0.7248[b] |
| 28 | 15 | 0.71930 | 1.39024 | ..... | ..... |
| 29 | 20 | 0.71352 | 1.40150 | 0.71349 | 0.7135[b] |
| 30 | 25 | 0.70768 | 1.41307 | ..... | ..... |
| 31 | 30 | 0.70177 | 1.42497 | ..... | 0.7019[b] |
| 32 | 35 | 0.69580 | 1.43719 | 0.69576 | ..... |
| 33 | 40 | 0.68976 | 1.44978 | 0.68979 | 0.6894[b] |
| 34 | 45 | 0.68367 | 1.46269 | ..... | ..... |
| 35 | 50 | 0.67751 | 1.47599 | ..... | 0.6764[b] |
| 36 | 55 | 0.67129 | 1.48967 | 0.67116 | ..... |
| 37 | 60 | 0.66501 | 1.50374 | 0.66501 | 0.6658[b] |
| 38 | 65 | 0.65866 | 1.51823 | ..... | ..... |
| 39 | 70 | 0.65226 | 1.53313 | ..... | 0.6532[b] |

[a] Seitz, Alterthum and Lechner.

[b] Young.

[c] Keyes and Felsing.

temperature, it was decided to use a series equation. The following equations represent the observed values to one part in seven thousand:

$$\delta = 0.73629 - 0.0011138t - 0.000001237t^2 \quad (2)$$

$$\delta = 0.73629 - 0.0011044t - 0.0000004772t^2 \quad (3)$$

Equation 2 holds for the densities above 0° and Equation 3 holds below 0°. It is believed that the densities are correct to at least one part in 7000.

**The Vapor Pressures.**—The vapor pressures were measured from —60° to +20°. Since the cathetometer was graduated to 0.02 mm., it is probable that the vapor pressures are not more accurate than 0.05 mm. At least two check observations were obtained for every temperature and in many cases more. The equation below, relating the vapor pressure to the temperature, shows good agreement with the observations to 0°.

Above 0°, however, there is a slight trend away from the observations. The equation cannot be expected to give accurate extrapolated values in spite of the good agreement with the observed values.

$$\log p = -(2168.599/T) + 13.882702 - 0.01814165\,T + 0.00001718195\,T^2 \qquad (4)$$

In the equation, $p$ is the vapor pressure in millimeters of mercury and $T$

TABLE III

OBSERVED VAPOR PRESSURES

| No. | Temp. °C. | Vapor pressure observed Mm. | V. p. calc. from Eq. 4 Mm. | No. | Temp. °C. | Vapor pressure observed Mm. | V. p. calc. from Eq. 4 Mm. |
|---|---|---|---|---|---|---|---|
| 1 | −60.799 | 3.95 | 3.91 | 10 | −16.578 | 80.67 | 80.65 |
| 2 | −55.748 | 5.93 | 5.96 | 11 | −11.637 | 104.79 | 104.87 |
| 3 | −50.873 | 8.77 | 8.76 | 12 | − 6.698 | 134.76 | 134.76 |
| 4 | −45.998 | 12.62 | 12.62 | 13 | + 0.009 | 186.13 | 186.18 |
| 5 | −41.125 | 17.78 | 17.85 | 14 | + 4.975 | 233.73 | 233.69 |
| 6 | −36.231 | 24.77 | 24.85 | 15 | 9.937 | 290.62 | 290.50 |
| 7 | −31.329 | 34.03 | 34.06 | 16 | 14.903 | 358.15 | 357.99 |
| 8 | −26.421 | 45.81 | 46.00 | 17 | 19.871 | 437.70 | 437.51 |
| 9 | −21.502 | 61.31 | 61.31 | .. | ...... | .... | .... |

TABLE IV

CALCULATED VAPOR PRESSURES

| No. | Temp. °C. | Temp. ° Abs. | Vapor pres. calc. | Vapor pres. of other observers |
|---|---|---|---|---|
| 1 | −65 | 208.135 | 2.70 | |
| 2 | −60 | 213.135 | 4.19 | |
| 3 | −55 | 218.135 | 6.32 | |
| 4 | −50 | 223.135 | 9.36 | |
| 5 | −45 | 228.135 | 13.57 | |
| 6 | −40 | 233.135 | 19.28 | |
| 7 | −35 | 238.135 | 26.93 | |
| 8 | −30 | 243.135 | 37.00 | |
| 9 | −25 | 248.135 | 49.94 | |
| 10 | −20 | 253.135 | 66.75 | 68.90[a]<br>62.99[b] |
| 11 | −15 | 258.135 | 87.82 | |
| 12 | −10 | 263.135 | 114.10 | 114.72[a]<br>111.81[b] |
| 13 | − 5 | 268.135 | 146.52 | |
| 14 | 0.000 | 273.135 | 186.10 | 184.39[a]<br>184.90[b] |
| 15 | + 5 | 278.135 | 233.95 | |
| 16 | 10 | 283.135 | 291.29 | 286.83[a]<br>291.78[b] |
| 17 | 15 | 288.135 | 359.41 | |
| 18 | 20 | 293.135 | 439.56 | 432.78[a]<br>442.36[b] |
| 19 | 25 | 298.135 | 533.78 | |

[a] Regnault.

[b] Young

is the absolute temperature. The value 273.135° for the ice point on the absolute scale was used for all calculations. The observed and calculated values are given in Table III.

In Table IV are given the values of the vapor pressure for every 5° over the interval measured. The values of Regnault and of Young are also given for comparison.

The apparatus described in this paper was not applicable for measuring vapor pressures above room temperature. It is noticed that the pressure obtained at 0° does not agree with that of Regnault or of Young. Since the zero point is most reproducible, this temperature was investigated very carefully with two different loadings of fresh ether and the values thus obtained agreed with the original one.

TABLE V

DERIVED QUANTITIES FOR ETHER

| No. | Temp. °C. | $V_1$ calc. from Eq. 6 | $V_1$ from other observers | $\lambda \frac{\text{cal.}}{\text{g.}}$ calc. from Clap. Eq. | $\lambda$ obs. | $\lambda - p(\Delta v)$ or $\Delta U$ in $\frac{\text{cal.}}{\text{g.}}$ | $C_{S_1} - C_{S_2}$ $\frac{\text{cal.}}{\text{g.°}}$ |
|---|---|---|---|---|---|---|---|
| 1 | −65 | 64927 | .... | 104.52 | ... | 98.94 | −.6932 |
| 2 | −60 | 42836 | .... | 103.56 | ... | 97.84 | −.6762 |
| 3 | −55 | 29034 | .... | 102.64 | ... | 96.78 | −.6601 |
| 4 | −50 | 20040 | .... | 101.62 | ... | 95.64 | −.6641 |
| 5 | −45 | 14128 | .... | 100.67 | ... | 94.56 | −.6291 |
| 6 | −40 | 10160 | .... | 99.74 | ... | 93.50 | −.6148 |
| 7 | −35 | 7426.9 | .... | 98.805 | ... | 92.43 | −.6010 |
| 8 | −30 | 5515.5 | 6127[19] | 97.890 | ... | 91.38 | −.5878 |
| 9 | −25 | 4166.7 | 4581[19] | 96.975 | ... | 90.35 | −.5750 |
| 10 | −20 | 3177.2 | 3484[19] | 96.073 | ... | 89.32 | −.5628 |
| 11 | −15 | 2459.6 | 2616[19] | 95.161 | ... | 88.28 | −.5508 |
| 12 | −10 | 1927.1 | 1992[19] | 94.265 | ... | 87.26 | −.5393 |
| 13 | − 5 | 1526.8 | 1551[19] | 93.378 | ... | 86.26 | −.5281 |
| 14 | 0 | 1222.3 | 1225.5[19]<br>1209.2[2] | 92.493 | 94.0[15] | 85.25 | −.5172 |
| 15 | + 5 | 987.9 | 953[19] | 91.603 | 93.5[16] | 84.25 | −.5066 |
| 16 | 10 | 805.63 | 763.4[19]<br>791.1[2] | 90.719 | 92.52[17] | 83.25 | −.4962 |
| 17 | 15 | 662.65 | 628.9[19] | 89.837 | 15.5°<br>89.25[15] | 82.26 | −.4860 |
| 18 | 20 | 549.49 | 526.3[19]<br>534.8[2] | 88.963 | 87.54[17] | 81.29 | −.4760 |
| 19 | 25 | 458.58 | 446.8[19] | 88.083 | ... | 80.31 | −.4661 |
| 20 | 0.138 | ..... | .... | ..... | 90.50[18] | ... | ..... |
| 21 | 11.813 | ..... | .... | ..... | 88.83[18] | ... | ..... |

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[15] Ramsay and Young, *Phil. Trans.*, **178A,** 329 (1887).

[16] Winkleman, *Wied. Ann.*, **9,** 208, 358 (1880).

[17] Mills, THIS JOURNAL, **31,** 1123 (1909).

[18] Beattie, unpublished *Thesis, Mass. Inst. Tech.*, **1918.**

[19] Battelli, *Ann. chim. phys.*, **6,** 25 (1892).

**Discussion of Data and Calculation of Derived Quantities.**—The Clapeyron equation[20]

$$\lambda = T\,(v_1 - v_2)\,\frac{\mathrm{d}p}{\mathrm{d}T} \qquad (5)$$

was used to calculate the latent heats of evaporation, $\lambda$. The values of the specific volume of the liquid ($v_2$) were obtained from Table II. The values of $v_1$ given in Table V were obtained from the perfect gas law and, for the higher temperatures, from the equation

$$p = \frac{RT}{v_1 - 6.25} - \frac{5796.2}{v_1^2} \qquad (6)$$

which is the equation given by Keyes and Felsing[5] simplified to the form of van der Waals' equation. The values of the specific volume of the vapor, $v_1$ given by various observers are also listed in Table V. The latter are erratic, indicating possibly that the equation of state gives values which are at least as reliable as the measured volumes. The values of Battelli[21] were plotted against the temperature to a very large scale and the volumes read at the even temperatures in order to compare them with the calculated values.

The rate of change of the vapor pressure with the temperature along the saturation curve was obtained from Equation 4 by differentiating, giving

$$\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\text{sat.}} = \left(\frac{4993.395}{T^2} - 0.04177279 + 0.0000791267T\right)p \qquad (7)$$

The values of the heat of vaporization, in calories per gram, calculated from the above, are given in Table V and were used to calculate the internal energy change which is also listed in Table V. The internal energy change was obtained by subtracting the pressure-volume work, $p\,\Delta v$, from the latent heat.

The thermodynamic equation,

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \qquad (8)$$

gives a general relation between the internal energy and the volume. From the Keyes[22] equation we obtain

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - \delta}$$

and Equation 8 becomes

$$\left(\frac{\partial U}{\partial v}\right)_T = \frac{RT}{v - \delta} - p = \frac{A}{(v + l)^2} \qquad (9)$$

---

[20] The subscript 1 refers to the vapor phase and the subscript 2 to the liquid phase in all the following discussion.

[21] Ref. 19, pp. 25, 38.

[22] Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917). $p = \dfrac{R}{v - \delta}\,T - \dfrac{A}{(v + l)^2}$

Hence the internal energy change from $v_2$ to $v_1$ is obtained by integrating Equation 9

$$\left[\Delta U = \int_{v_2}^{v_1} \mathrm{d}U = \int_{v_2}^{v_1} \frac{A}{(v+l)^2}\,\mathrm{d}v = A\left(\frac{1}{v_2+l} - \frac{1}{v_1+l}\right)\right]_T \qquad (10)$$

Equation 10 is true, provided the liquid phase is composed of the same type of molecules as the vapor phase or it might still be true if the molecules of the liquid were all doublets and the vapor specific volume large enough to make the term $\frac{A}{v_1+l}$ negligible. The change in internal energy on evaporation might, therefore, be accurately represented by an equation of the form

$$\Delta U = \frac{A}{v_2+l}$$

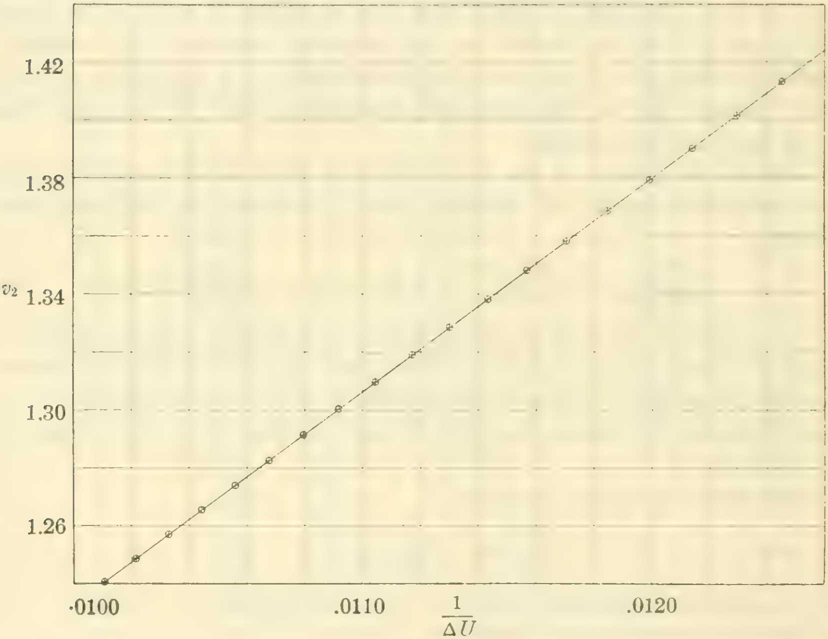

Fig. 5.

where $v_1$ is large. More conveniently arranged

$$\frac{1}{\Delta U} = \frac{v_2}{A} + \frac{l}{A} \qquad (11)$$

Equation 11 is linear in $v_2$ and $1/\Delta U$. The plot given in Fig 5 shows how closely this deduction holds. The equation for the straight line drawn in Fig. 5 is

$$\frac{1}{\Delta U} = \frac{v_2}{73.423} - 0.006791 \qquad (12)$$

where $\Delta U$ is in calories per gram and $v_2$ in cc. per gram.

Some information on the difference in specific heats of the saturated vapor and liquid may be obtained from the observed and derived quantities given above. The logarithm of the latent heat was plotted against the logarithm of the absolute critical temperature minus the absolute temperature. This gives almost a straight line. The equation of this curve, shown in Fig. 6, was obtained.

$$\log \lambda = 3.165779 - 1.423343 \log (T_c - T) + 0.3939349 [\log (T_c - T)]^2 \quad (13)$$

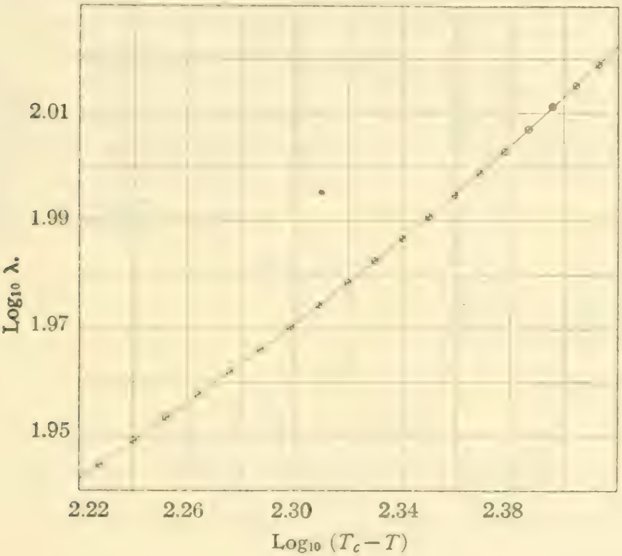

Fig. 6.

Equation 13 when differentiated gives

$$\left(\frac{d\lambda}{dT}\right) = [1.42334 - 0.78587 \log (T_c - T)] \frac{\lambda}{(T_c - T)} \quad (14)$$

By means of the thermodynamic equation

$$C_{s_1} - C_{s_2} = \left(\frac{d\lambda}{dT}\right) - \frac{\lambda}{T} \quad (15)$$

the difference in saturation specific heats of the vapor and liquid may be calculated. These values are given in Table V. If the specific heat of one phase is known, the value for the other phase may be obtained.

Battelli,[23] Regnault,[24] Hartung,[25] S. Lussano,[26] and Beattie[18] have measured the specific heat of liquid ether. Regnault gives the equation

$$C_{s_2} = 0.529 + 0.000592t$$

where $t$ is degrees centigrade and $C_{s_2}$ is in calories per gram per degree. The values of these observers, together with the values for every 10°

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[23] Battelli, Landolt-Börnstein, "Tabellen," 1912.

[24] Ref. 1, p. 262.

[25] Hartung, *Trans. Faraday Soc.*, **11**, 64 (1915).

[26] S. Lussano, *Nuovo cimento*, **7**, 304 (1914).

calculated from Regnault's equation, are given in Table VI. Since Regnault's equation seems to represent the data fairly well, it was used to calculate the specific heats of the liquid phase.

TABLE VI

SPECIFIC HEATS OF ETHER

| Temp. °C. | $C_{s_2} \equiv C_{p_2}$ Obs. | Observer Ref. no. | $C_{p_1}$ calc. | $C_{p_1}$ obs.[28] |
|---|---|---|---|---|
| −50 | 0.517 | [23] | ... | ... |
| − 2 | 0.523 | [23] | ... | ... |
| −40 | 0.505 | [24] | 0.317 | ... |
| −30 | 0.511 | [24] | 0.325 | ... |
| −20 | 0.517 | [24] | 0.337 | 0.355 |
| −10 | 0.523 | [24] | 0.349 | 0.364 |
| 0 | 0.529 | [24] | 0.361 | 0.372 |
| 10 | 0.535 | [24] | 0.373 | 0.381 |
| 20 | 0.541 | [24] | 0.386 | 0.390 |
| 25 | 0.544 | [24] | 0.393 | 0.394 |
| 18.5 | 0.541 | (obs. 17° to 20°)[25] | ... | ... |
| 22.7 | 0.540 | [26] | ... | ... |
| 1.164 | 0.574 | [18] | ... | ... |
| 13.367 | 0.583 | [18] | ... | ... |

In the equation

$$C_{p_1} - C_{p_2} = C_{s_1} - C_{s_2} + T\left(\frac{\partial p}{\partial T}\right)_{\text{sat.}}\left[\frac{\partial v_1}{\partial T} - \frac{\partial v_2}{\partial T}\right]_p \qquad (16)$$

the value of $C_{s_2}$ is given from Regnault's data, the value of $C_{s_1} - C_{s_2}$ is obtained from Table VI, and $\left(\frac{\partial p}{\partial T}\right)_{\text{sat.}}$ from Equation 7.

The expression for $\left(\frac{\partial v_1}{\partial T}\right)_p$ was obtained by differentiating equation (6) and is

$$\left(\frac{\partial v_1}{\partial T}\right)_p = \frac{v-\beta}{T}\left(\frac{1}{1 - \frac{2A}{RT}\left[\frac{(v-\beta)^2}{v^3}\right]}\right)$$

$\left(\frac{\partial v_2}{\partial T}\right)_p$ as given by Tyrer[27] is 0.0020 at 0° and hence could be neglected in the calculations without introducing any error.

The values of $C_{p_1}$ calculated from this equation are also given in Table VI. E. Wiedmann[28] gives the equation $C_p = 0.3725 + 0.0008536t$ for the specific heat of the vapor. Values calculated from this equation are given in Table VI. Of course the calculated values cannot be very accurate since $d\lambda/dT$ contains the second derivative of $p$ as a factor and $\lambda/T$ contains the first derivative. Moreover, the values of $C_{s_2}$ are not very accurate.

In conclusion, we desire to thank Professor Keyes of this Laboratory at whose suggestion the investigation was started and whose advice and assistance were of great help during its progress.

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[27] Tyrer, *Z. physik. Chem.*, **87**, 175 (1914).

[28] Wiedmann, *Wied. Ann.*, **2**, 195 (1877).

## Summary

1. The densities and vapor pressures of ether have been measured over the lower temperature range.

2. From these and an equation of condition, the latent heats of evaporation and the change in internal energy on evaporation were calculated.

3. A relation connecting the specific volume of the liquid and the internal energy change on evaporation is given.

4. From the latent heats there was obtained the difference in saturation specific heats of the vapor and liquid, and from these, when compared with Regnault's values for the liquid, some values of the specific heat of the vapor at constant pressure were deduced.

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## The Activities of the Ions of Potassium Hydroxide in Aqueous Solution

by

M. Knobel

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# THE ACTIVITIES OF THE IONS OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION

By M. Knobel.

Received September 23, 1922

## Introduction

This work is a revision of that of Chow[1] on the measurement of the electromotive force of concentration cells of potassium hydroxide for the purpose of determining the activities of the ions. Chow's results were based on single measurements for each pair of concentrations and were made with a form of electrode which has since been found to be unreliable.

The principle involved is the same as that used by MacInnes and Parker[2] on potassium chloride solutions, by Ellis, and Noyes and Ellis[3] on hydrochloric acid and by MacInnes and Beattie[4] on lithium chloride. The cells were of the type, $H_2 \mid KOH\ (c_1) \mid KHg_x \mid KHg_x \mid KOH\ (c_2) \mid H_2$, in which the net effect of passing 1 faraday from left to right is the transfer of one mole of potassium hydroxide from a concentration $C_1$ to a concentration $C_2$. The electromotive force is given by the expression.[2] $E = 2\,RT/F\ ln\ \alpha_1 C_1/\alpha_2 C_2$ where $\alpha_1$ and $\alpha_2$ are the mean activity coefficients of the two ions in the two solutions of concentration $C_1$ and $C_2$, respectively; $R$, $T$, and $F$ have the usual significance.

## Apparatus

The apparatus used is shown in Fig. 1. The amalgam was contained in the vessel A and was run into the cell through the capillary tubes B. This form of electrode was found by Chow[1] and Beattie[4] to be preferable to the cup electrode used by MacInnes and Parker.[2] The amalgam dropped into the bent arms D and overflowed into the vessel E which was open to the atmosphere. A difference of level of the mercury in D kept the solution from flowing out. The potassium hydroxide solutions, which were contained in the flasks G, flowed in through the tubes H to the cell and out through the tubes J into the bottle L. The rate of flow of the solutions was determined by the pinchcocks T. L was nearly filled with nitrogen at atmospheric pressure at the start. The tubes M, which allowed gas to flow into the space above the solutions in the flasks G, maintained atmospheric pressure in the flasks, for as solution ran out of G into L, an equal volume of gas was displaced through tubes M into the top of G. This equalization of pressure was a very necessary condition in order to maintain atmospheric pressure in the hydrogen electrodes $N_1$ and $N_2$, which were connected as shown with the central tubes $C_1$ and $C_2$. The hydrogen electrodes consisted of 3 platinized platinum gauze strips connected through a glass seal in the tubes passing through the rubber stopper. The hydrogen, which was first bubbled through some of the same solution as contained in the cell, was led in by the tubes P and out by R which prevented air from diffusing back. No water seal was necessary as long as the gas was kept bubbling at a moderate rate.

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[1] Chow, This Journal, **42**, 488 (1920).

[2] MacInnes and Parker, *ibid.*, **37**, 1445 (1915).

[3] Ellis, *ibid.*, **38**, 737 (1916). Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[4] MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).

The whole apparatus was held in a frame and placed in a thermostat with the water level nearly up to the tops of the tubes C. A high quality of commercial potentiometer was used to measure the electromotive force, and was standardized by 2 standard cells which had just been received from the Bureau of Standards. The temperature of the thermostat water was maintained at 25° within 0.02°.

## Method of Procedure

The method of making the measurements was as follows. The flasks G of Fig. 1 were filled with nitrogen and then with the respective potassium hydroxide solutions of the 2 concentrations, care being taken to exclude air completely. The hydrogen electrodes were washed several times with their respective solutions and set in place after the tubes C and N had been filled. The amalgam container A was filled from a reservoir. The tubes $C_1$ and $C_2$ were filled to the top by increasing the pressure in $N_1$ and $N_2$ slightly and the stoppers on the tubes B of the amalgam container put in place so that no gas remained in the tops of $C_1$ and $C_2$. Hydrogen was then passed in to bring the electrodes to equilibrium, which usually occurred in 1/2 to 1 hour. When 3 *N* potassium hydroxide solution was used, however, nearly 3 hours was necessary to attain equilibrium.

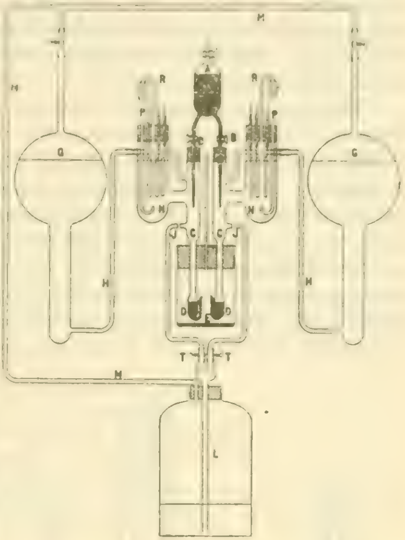

Fig. 1.

After this equilibrium was established the flow of the solutions was started at the rate of about 80 cc. per minute, by opening the pinchcocks T, and the amalgam was run in through the fully opened stopcocks in tubes B at the rate of about 1 cc. per minute. Hydrogen was allowed to bubble in continuously and rapidly enough to prevent air from being sucked back when the level dropped in $N_1$ and $N_2$, as it did slightly. This slight change of level did not affect the hydrogen electrodes, for they checked as well after the run as before. Measurements of the electromotive force were made between one hydrogen electrode of $N_1$ and one of $N_2$. The time of the run was from 4 to 5 minutes and measurements were taken continuously. The potential usually stayed constant to 0.1 millivolt for about 3 minutes, after which it varied up or down. In some cases it was constant for the entire run.

## Preparation of Materials

The potassium amalgam was made by electrolyzing potassium into pure mercury from a solution of pure potassium hydroxide. The amalgam was then separated from the solution as completely as possible by passage through a capillary tip, and then placed in a 500cc. Pyrex flask, provided with a capillary stopcock. The flask was sealed and allowed to stand for 2 or 3 days to dry. The amalgam contained approximately 0.2% by weight of potassium. Amalgams of 0.02% and 0.002% by weight were made by dilution of the 0.2% solution with pure mercury. These were also kept in sealed containers provided with stopcocks. Potassium hydroxide contaminated the amalgam in the containers but when the amalgam was drawn off through the capillary stopcocks it came out almost as clean as pure mercury.

The more dilute amalgam was used with the dilute solutions and the more concentrated amalgams with the more concentrated solutions. The electromotive force is independent of the concentration of the amalgam provided it is the same in both cells, but it was found that the electromotive force was much steadier when this approximate adjustment of amalgam concentration to solution concentration was made. The most concentrated amalgam, when used with the 0.01 and 0.001 *N* solutions, gave an electromotive force value which averaged about that obtained with the dilute amalgam, but it was very unsteady.

The potassium hydroxide solutions, with the exception of the 3 *N* solutions, were prepared in the apparatus shown in Fig. 2. This consists of two Pyrex flasks A and B of 1 liter and 3 liters capacity, respectively, joined by a 12mm. tube as near the bottom as possible. About 500 cc. of pure dry mercury was used, sufficient to fill well above the connecting tube. The 3-liter flask was first evacuated, then filled with nitrogen, and finally with conductivity water (collected hot and boiled under reduced pressure) which was forced in, out of contact with air and while still hot. A very strong solution of pure potassium hydroxide was next added to flask A, which was fitted as a simple electrolytic cell. Potassium was electrolyzed into the mercury as cathode. The current was usually limited to 2 or 3 amperes, as too strong a current gave a concentrated viscous amalgam. More potassium hydroxide solution was added as it was used up. The whole apparatus was mounted in a box and rocked back and forth (about one cycle in 10 seconds), thus circulating the amalgam produced in A throughout B. The decomposition of the amalgam in B was aided by the platinized platinum electrode E which was short circuited with the amalgam. This electrode was, in fact, necessary to produce reasonably rapid solution of the potassium. To prevent air from entering B the water seal C was used. This was made as shown to allow for the large fluctuations in volume as the mercury flowed back and forth between the flasks A and B. Five to 6 days were necessary to produce a 1 *N* solution. This apparatus gave an exceptionally pure solution of potassium hydroxide. A test with barium hydroxide showed the absence of carbonate, and there must have been a minimum of dissolved air since at no time did the solution come in contact with the atmosphere, and hydrogen was constantly forming at the electrode E. The solutions, which were perfectly clear, were withdrawn from the electrolyzer into a flask fitted with a short tube and one reaching to the bottom resembling a wash bottle.

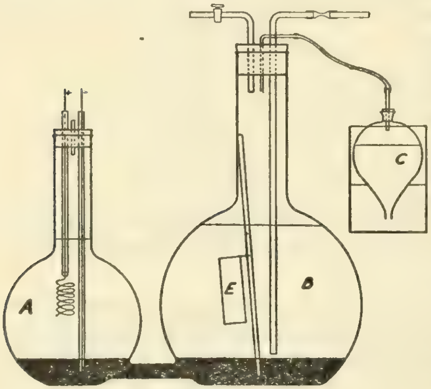

Fig. 2.

The 3 *N* solutions were made from a solution of the purest potassium hydroxide obtainable,[5] by adding solid barium hydroxide to precipitate the carbonate. Tests were made for carbonate at frequent intervals and when it had all been precipitated and a slight excess of barium was present, the solution was filtered. The small excess of barium was precipitated while filtering and a final solution obtained which gave no test for either carbonate or barium. This solution was then boiled for over an hour under reduced pressure to free it from dissolved air. The presence of oxygen in the concentrated solutions is not so harmful, however, as in the dilute solutions. Further, two determinations of the electromotive force of the cell with solutions made by electrolysis and by precipitation checked within the experimental error.

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[5] A commercial quality "purified by alcohol."

These conc. solutions were analyzed as follows. A weighed quantity (30 to 40 g.) was titrated nearly to the end-point by a weighed quantity of constant-boiling hydrochloric acid which had been standardized to 0.01% by precipitation of the chloride as silver chloride. The small amount of residual base was titrated with approximately 0.03 *N* acid, using methyl red as indicator. In general, but a few cubic centimeters of these solutions were necessary, so that the accuracy of weighing determined the accuracy of analysis. Results that check more closely than within 0.05% were consistently obtained.

Other solutions were made by gravimetric dilution of one of the strong solutions with hot conductivity water. All manipulation was performed out of contact with air, in flasks resembling wash bottles with stopcocks in each arm, and all solutions were boiled under reduced pressure before the final weighing. They were kept in an atmosphere of nitrogen, and were never allowed to stand for more than 4 days before use, and frequently not longer than one day. However, no difference was found between solutions 4 days old and 1 day old, as shown by two determinations of the electromotive force made to test this point.

## Measurements

Fifteen successful sets of measurements were made, giving 7 determinations which were checked once and in one case twice. The check measurements were in every case made with solutions for which separate analytical data were obtained. The results are given in Table I. The concentrations were within 2 to 3% of round numbers and activity coefficient ratios were calculated with these values. The concentrations in moles of potassium hydroxide per 1000 g. of water are given in the first two columns. The measured electromotive force is given in the third

TABLE I

ELECTROMOTIVE FORCES OF POTASSIUM HYDROXIDE CONCENTRATION CELLS AT 25°

| Concentrations Moles KOH per 1000 g. of $H_2O$ | | Measured e.m.f. | Activity-coeff. ratio |
|---|---|---|---|
| $C_1$ | $C_2$ | $E$ | $\frac{\alpha_1}{\alpha_2}$ |
| 3.000 | 0.2915 | 0.1416 | 1.530 |
| 2.955 | 0.2963 | 0.1395 | 1.515 |
| 0.992 | 0.0996 | 0.1172 | 0.983 |
| 0.995 | 0.0992 | 0.1170 | 0.972 |
| 0.992 | 0.0996 | 0.1169 | 0.977 |
| 0.300 | 0.0998 | 0.05361 | 0.945 |
| 0.300 | 0.1000 | 0.05345 | 0.943 |
| 0.2963 | 0.0282 | 0.1138 | 0.872 |
| 0.3000 | 0.0299 | 0.1110 | 0.865 |
| 0.0992 | 0.00989 | 0.1110 | 0.865 |
| 0.0996 | 0.00984 | 0.1110 | 0.857 |
| 0.0288 | 0.00286 | 0.1120 | 0.879 |
| 0.0299 | 0.00293 | 0.1130 | 0.882 |
| 0.0100 | 0.000991 | 0.1147 | 0.924 |
| 0.0100 | 0.001000 | 0.1149 | 0.936 |

column, and the activity coefficient in the fourth, calculated from the equation, $E = 2RT/F \ ln \ \alpha_1 C_1/\alpha_2 C_2 = 0.1183 \log \alpha_1 C_1/\alpha_2 C_2$, where $R$, the gas constant, is taken as 8.316, $T$ as 298.1, and $F$ as 96,500.

The activity-coefficient ratios calculated in this manner are not directly comparable on account of the differences in concentrations. They were corrected to even concentrations by the following method. A curve was plotted of activity against the square root of the concentration (the latter being used instead of the concentration itself in order to reduce the size of the plot), using values from determinations in which the concentrations were nearest to round numbers. This gave the slope of the curve with more accuracy than sufficient to find the correction which must be added or subtracted to give the activity coefficient at the nearest round number. The maximum concentration difference to be corrected was only 6% and a difference of 1% in the concentration in general affected the activity-coefficient ratio to less than 0.1%. In Table II these mean values are given. There are also included in this table the values of the free energies of dilution for the approximate concentrations indicated.

TABLE II

ACTIVITY-COEFFICIENT RATIOS AND FREE ENERGY OF DILUTION OF POTASSIUM HYDROXIDE AT 25°

| Concentrations Moles of KOH per 1000 g. of $H_2O$ | | Mean activity-coeff. ratio | Free energy of dilution |
|---|---|---|---|
| $C_1$ | $C_2$ | $\frac{\alpha_1}{\alpha_2}$ | $F$(joules) |
| 3.0 | 0.30 | 1.522 | 13,500 |
| 1.0 | 0.10 | 0.978 | 11,300 |
| 0.30 | 0.10 | 0.944 | 5,160 |
| 0.30 | 0.03 | 0.870 | 10,730 |
| 0.10 | 0.01 | 0.861 | 10,670 |
| 0.03 | 0.003 | 0.880 | 10,780 |
| 0.01 | 0.001 | 0.930 | 11,060 |

To find the activity coefficient itself we must make some assumption in regard to the relation of activity and concentration at some one point. We assumed, therefore, that the activity is equal to the "concentration" of the ions in the most dilute solution (0.001 $N$), the "concentration" being computed in the familiar manner from conductance data. The ionization at 0.001 $N$ was derived from the equivalent conductance value of Kohlrausch[6] and the conductance at infinite dilution given by Johnston[7] which results in the figure 0.989. Using this value the activity coefficients given in Table III, second column, were calculated. The third column of Table III contains the activity coefficients determined by Chow.[1] In the fourth column are given the conductance ratios, using again Kohlrausch's values, and the fifth column contains the conductance-viscosity ratio, using the viscosity data of Kanitz.[8]

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[6] Kohlrausch and Holborn, "Das Leitvermögen der Elektrolyte," B. G. Teubner, 1916.

[7] Johnston, THIS JOURNAL, 31, 1010 (1909).

TABLE III

MEAN ACTIVITY COEFFICIENTS OF THE IONS OF POTASSIUM HYDROXIDE AT 25°

| Concentrations Moles of KOH per 1000 g. of $H_2O$ | Activity coeff. | Activity coeff. (Chow) | Conductance ratio | Conductance-viscosity ratio |
|---|---|---|---|---|
| 3.0 | 1.136 | ... | 0.593 | (0.871)[a] |
| 1.0 | 0.775 | 0.793 | 0.776 | 0.877 |
| 0.3 | 0.748 | 0.769 | 0.855 | 0.889 |
| 0.1 | 0.792 | 0.846 | 0.900 | 0.910 |
| 0.03 | 0.857 | 0.920 | 0.936 | 0.939 |
| 0.01 | 0.920 | 0.961 | 0.962 | 0.963 |
| 0.003 | 0.974 | 0.982 | 0.980 | 0.980 |
| 0.001 | 0.989 | ... | 0.989 | 0.989 |

[a] Value for viscosity extrapolated from 2 *N* to 3 *N*.

It should be noted that this activity coefficient is the square root of the product of the activity coefficients of the two ions and equal to that of either ion only when the activities are equal.

## Discussion of Results

It is seen that there is a great difference (2 to 8%) between our values and those of Chow.[1] We believe that this is due principally to his having taken insufficient care to exclude air from his solutions. It is exceedingly important to have no dissolved oxygen in the solution, for oxygen reacts with the potassium of the amalgam, decreasing its concentration and at the same time increasing the concentration of the solution. The percentage effect is greater in the dilute solutions which, therefore, produce a smaller measured electromotive force and hence smaller activity ratio; Chow's results are in this direction.

Chow also used mercuric oxide electrodes instead of hydrogen electrodes and the former appear to be unreliable. For example, it was found by the present author that when the mercuric oxide was shaken with the potassium hydroxide for one week instead of one day, which was Chow's procedure in obtaining the equilibrium mixture for the electrodes, a difference in the electromotive force of from 1 to 6 millivolts was observed. There are 2 forms of mercuric oxide, red and yellow, and they have different solubilities and hence different free energies.[9] The yellow form, which consists of the smaller particles, is the more soluble. When red mercuric oxide is shaken with potassium hydroxide it slowly changes over to a certain extent to the yellow form and at a rate dependent on the concentration of the potassium hydroxide. In strong alkali (1.0 *N*), the change is comparatively slow; in 2 weeks there is hardly a perceptible

[8] Kanitz, *Z. physik. Chem.*, **22**, 340 (1897).

[9] Fuseya, THIS JOURNAL, **42**, 368 (1920).

change in color, but it is decidedly evident after 2 months. In the more dilute solutions (for example, in 0.001 *N*), however, shaking overnight is sufficient to change an appreciable amount of the red to the yellow form. The rate of change of one form to the other appears to be roughly inversely proportional to the concentration of the alkali. With this variable factor it can be readily seen that no true equilibrium can be expected. Even if each were shaken long enough to attain equilibrium, the difference of the free energies of the mercuric oxide on the two sides of the cell would invalidate the resultant electromotive force. The constancy of the potential of the cell, $H_2 | KOH | HgO | Hg$, with change in the concentration of the potassium hydroxide, obtained by Chow,[1] can probably be explained by the fact that too short a time of shaking the mercuric oxide with the alkali was allowed, so that the red form had not yet changed to the yellow.

It is seen that the degree of ionization and the activity coefficient are far from equal except at very low concentrations and in a small range at 1.8 *N* where the activity-coefficient curve rises again. The minimum at 0.42 *N* has an activity coefficient 19% less than the "degree of ionization" and at 3.0 *N* the activity coefficient is 30% greater. The curve has the typical form found by other investigators for the uni-univalent type of electrolyte, resembling most nearly that of lithium chloride.

The activity coefficients given in Table III are estimated to be reliable to 0.5% on the average, the maximum divergence between the corrected activity-coefficient ratios for the two runs on the same concentrations being 0.6%.

Sincere appreciation is rendered Dr. D. A. MacInnes for his kind help and suggestions during the course of this work.

## Summary

The electromotive forces of cells of the type, $H_2 | KOH\ (c_1) | KHg_x | KHg_x | KOH\ (c_2) | H_2$, have been measured at 25° for concentrations of potassium hydroxide ranging from 3 *N* to 0.001 *N*. The activity coefficients of the ions of the solution at various concentrations and the free energy of dilution between various concentrations have been calculated and tabulated. Data given by Chow[1] have been found to be incorrect.

The relation between the activity and concentration for potassium hydroxide has been found to be similar to that for other uni-univalent electrolytes.

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# A STUDY OF THE MOVING BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS

by

Duncan A. MacInnes and Edgar Reynolds Smith

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# A STUDY OF THE MOVING BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS

By Duncan A. MacInnes and Edgar Reynolds Smith

Received June 27, 1923

In our study of solutions of strong electrolytes it became desirable to obtain accurate transference numbers of a number of salts throughout a range of concentrations. From its apparent precision and the rapidity with which the measurements can be made, the moving boundary method for obtaining these numbers seemed attractive, and a careful study of the method was accordingly undertaken.

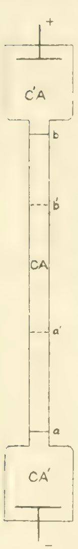

Fig. 1

As usually described, the moving boundary method for determining transference numbers is as follows. The transference number of one of the two ions of a salt is equal to the distance moved by the boundary of one of the ion constituents divided by the distances moved in the same time and under the same potential gradient by the boundaries of both ion constituents. These distances can be measured in an apparatus shown diagrammatically in Fig. 1. A solution of the salt CA under investigation is placed between one of CA′ and another of C′A, having, respectively, the same cation and anion as the salt CA. The boundary at *a* and that at *b* are visible because of the different refractive indices of the solutions. On passing current through the apparatus the boundary *a* moves up to *a*′ and the boundary *b* moves down to *b*′. The ratio: $aa'/(aa' + bb')$ is equal to the transference number $T_a$ The solution of C′A must be lighter, and that of CA′ heavier, than the solution of CA, and the ions C′ and A′ have smaller mobilities than the ions C and A, respectively, in order that the boundaries shall persist during the passage of current. The apparatus can also be constructed in the form of a U-tube, in which case both of the following or indicator solutions must be lighter than the solution whose transference number is being measured.

Aside from the purely qualitative early work by Lodge[1] and others, the only workers who have published measurements made by this method are Denison and Steele,[2] and later Denison.[3] These workers obtained a large amount of transference data including measurements on most of the more common strong electrolytes at various concentrations.

The authors of the present article have made an endeavor to extend and amplify Denison and Steele's work. In the first part of the investigation, after obtaining sharp and readily visible boundaries (which proved to be by no means easy), it was found that, although precise measurements could be obtained, the results were not reproducible unless all possible variables, such as impressed e.m.f. and the kind and the concentrations of the salts forming the indicator solutions, were kept constant. Also, the results obtained departed widely and erratically from the accepted values of the transference numbers. A single instance of the difficulties encountered will suffice. Measurements were made on a 0.1 $N$ solution of potassium chloride, using 0.1 $N$ lithium chloride and potassium acetate solutions as indicators. The "transference numbers" at 135, 230 and 325 volts were 0.638, 0.550 and 0.531, respectively. These values were reproducible to about 0.1% at each voltage, though they all depart widely from the correct value, 0.508.[4] It is interesting to note that the values approach nearer to the correct number for the higher potentials. A change of the nature or concentrations of the indicator solutions leads to quite different results from those given.

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[1] Lodge, *Brit. Assoc. Repts., Birmingham,* **1886,** p. 389.

[2] Denison and Steele, (a) *Phil Trans.,* (A) **205,** 449 (1906); (b) *Z. physik. Chem.,* **57,** 110 (1906–7).

[3] Denison, *Trans. Faraday Soc.,* **5,** 165 (1909).

From these and many other similar discouraging results it became quite evident that either the method was useless or some additional factor must enter. In correspondence with Professor Denison he suggested that the concentrations of the indicator solutions should be adjusted according to the relation,

$$C/T = C'/T' \tag{1}$$

in which $C$ and $T$ are the concentration and the transference numbers of the solution under observation and $C'$ and $T'$ are the corresponding values for the indicator solution. Kohlrausch,[4] in an early paper, derives this relation as a necessary condition for a stable moving boundary. He states, however, that the condition represented by that equation will automatically be established, if not present at the outset, from which it would be concluded that the initial concentration of the indicator solution is of little importance. Later, it was given a simpler derivation by Denison.[5] Denison and Steele[2a] also state that the condition represented by Equation 1 establishes itself automatically, and give no limits to this spontaneous adjustment. These authors say, "It has been proved that the concentration of the lithium chloride (indicator solution) becomes automatically adjusted, so that the potential gradient is just sufficiently increased to make the lithium ions keep pace with the potassium ions," the latter being the ions of which the transference number is wanted. Denison[5] has shown in his derivation that, under the conditions given, Equation 1 holds.

It became of interest to us therefore to determine (a) whether the boundaries move at the theoretical velocities if the condition given in Equation 1 is fulfilled at the boundaries, and (b) whether any of the automatic adjustment, predicted by Kohlrausch, takes place. It is evident that if the concentrations of the solutions must be *exactly* adjusted according to the ratio given by Equation 1, the moving boundary method is useless for obtaining transference numbers, since these numbers, as well as those of the indicator solutions at a series of concentrations, must be known in advance. On the other hand, if there is even a small amount of the automatic adjustment predicted by Kohlrausch the correct transference numbers can be arrived at as the result of a series of experiments which approximate, more and more closely, to the theoretical conditions. This will be discussed more fully, later.

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[4] Kohlrausch, *Ann. Physik*, **62**, 209 (1897).

[5] Denison, *Z. physik. Chem.*, **44**, 581 (1903). See also Miller, *ibid.*, **69**, 436 (1909).

Because of a reduction of the number of variables and the ease of practical manipulation the apparatus we finally used involved only one moving boundary. If the current through the apparatus is kept constant throughout the experiment the transference number can be computed with as great accuracy as from the movement of two boundaries, provided, of course, that the boundary moves at the rate required by the theory under the conditions of the experiment.

The equations involved in the computation of the ionic mobilities and transference numbers when only one boundary is used are obtained as follows: If $V$ is the velocity with which the ion constituent moves and $U_1$ its mobility, and $\epsilon$ the potential gradient then

$$V = U_1\epsilon \qquad (2)$$

Now the current through the tube, $i$, is determined by Equation 3, in which $C$ is the concentration, $A$ the area of tube and $F$ the Faraday equivalent;

$$i = (U_1 + U_2)\, \epsilon\, CAF \times 10^{-3} = \epsilon\kappa A \qquad (3)$$

since the specific conductance, $\kappa = (U_1 + U_2)CF \times 10^{-3}$. From (2) and (3) then

$$U_1 = V\kappa A/i = l\kappa A/i\,t \qquad (4)$$

in which $l$ is the distance along the tube moved by the boundary in the time $t$.

From the mobility $U_1$ the transference number can, of course, be computed, but the transference number can also be computed from the measurements without a knowledge of the specific conductance, since

$$V = U\epsilon = T\Lambda\epsilon/F$$

now $\epsilon = i/\kappa A$ and $\Lambda = 1000\kappa/C$, therefore,[6]

$$T = VCFA/1000i = lCFA/1000\,it \qquad (5)$$

## Apparatus and Procedure

The cell shown in Fig. 2 was used for the study of the individual mobility of an ion constituent and the determination of transference numbers by the single boundary method.

Let us consider the case of the measurement of the mobility of the potassium-ion constituent in a solution of potassium chloride. The electrode vessel $D$ and measuring tube $T$ are filled with the potassium chloride solution, which is kept out of

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[6] Since $lA$ is the volume swept through during the time $t$, and $i\,t$ is the number of coulombs, the transference number can be found by measurement with one boundary and a measurement with a coulometer in series, a principle we may make use of in future work.

*B* and *A*, and the combination ground glass stopper and electrode tube *C* is put firmly in place. In this case the electrode *E* is a piece of platinum gauze plated electrolytically with silver and then covered with silver chloride by electrolysis. This ground glass stopper *C* was used instead of rubber because the latter, when pushed strongly into the tube, may undergo a slow expansion which would influence the motion of the boundary. The glass rod *R* has a flat circular enlargement, *B*, on the lower end, which is tipped with a circular disk of thin rubber held on by a small central spot of de Khotinsky cement. This rod, which slides easily through the hole in the rubber stopper, is next pressed firmly over the top of *T* and the entrapping of air bubbles under it is avoided. Any excess of solution squeezed out of *T* and into *B* by this action is removed by a capillary pipet thrust through one of the openings, marked *O*, in the rubber stopper. The electrode vessel *A* is then filled with lithium chloride solution and the anode *F*, which consists of a platinum gauze electroplated with silver, is inserted. The apparatus is next placed in a glass walled thermostat (regulated to 25° ± 0.05°), and the connections to the source of voltage are made. Then lithium chloride solution is pipetted through one of the openings marked *O* until *B* is filled. *R* is then gently loosened, but not yet pulled up, so that several milliamperes pass. The boundary between the lithium and potassium ions at once starts down the tube *T*. After the boundary has advanced about a centimeter the rod *R* is carefully pulled up. It was found possible to discard entirely the parchment paper used at the point corresponding to *B* in Denison and Steele's apparatus. The use of this paper is quite objectionable as it soaks up, from the tube *T*, solution which is afterward released into the indicator solution.

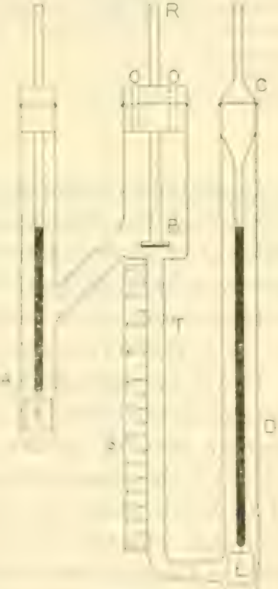

Fig. 2

The boundary was rendered visible by means of an arrangement similar to that used by Denison and Steele. A sheet of white paper was fastened on a frame and placed behind the thermostat. Two electric light bulbs were put behind the paper. By means of a cord and pulley a piece of black cardboard could be raised and lowered between the illuminated paper and the back of the thermostat. When the cardboard was raised to a position just below the boundary the latter became visible and could be read, on the scale *S*, readily to 0.1 millimeter.

The current through the tube, which was of the order of a few milliamperes, was maintained constant, within a few tenths of a per cent. by hand regulation of a rheostat in the circuit. Its value was known from the potential drop, measured with a potentiometer, across a standard resistance. The regulation was effected by observation of the scale of the galvanometer connected with the potentiometer. The source of current was a storage battery yielding 90 volts, to which was occasionally added a battery of dry cells. The volumes, corresponding to readings of the scale *S* in the tube *T* were obtained by means of a calibration with mercury. The length of *T* effective for measuring the motion of the boundary was 9 cm. and the scale *S* was graduated in millimeters. The position of the boundary could be estimated to the nearest 0.1 mm., so the precision of measuring the distance moved by the boundary was 0.2% or better.

## The Experimental Results

All the figures obtained in a single experiment, with the apparatus just described, are given in Table. I These results show the constancy of the velocity of the boundary during its whole passage down the tube, provided a constant current is sent through the apparatus. All the results given later in this article are averages of figures obtained as in this typical experiment and having about the same experimental accuracy. In making the readings times were read on the second that the boundary passed a given line on scale *S*.

TABLE I

TYPICAL EXPERIMENTAL RESULTS IN THE DETERMINATION OF A TRANSFERENCE NUMBER

Solution, 0.1 *N* KCl; indicator solution, 0.065 LiCl; current, 0.005893 amp.; potential gradient, in KCl solution, 4 volts per cm.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Scale reading | 0.50 | 5.50 | 5.80 | 6.10 | 6.40 | 6.70 | 7.00 |
| Time, sec. | 0.0 | 1900 | 2016 | 2130 | 2243 | 2357 | 2472 |
| Velocity, cm./sec., $\times 10^3$ | .. | 2.632 | 2.629 | 2.635 | 2.630 | 2.630 | 2.629 |
| | | | | | Av. velocity | | $2.631 \times 10^{-3}$ |
| | | | | | Av. mobility | | $0.6578 \times 10^{-3}$ |

In all the experiments the cathode side of the apparatus was closed in order that there might be no movement of the boundary arising from changes of level of the solution due to the electrolysis. It is necessary, however, as G. N. Lewis[7] has pointed out, to consider a correction for the volume change at the cathode during the passage of the current. However, at 0.1 *N* this correction is only one part in 5,000 for both salts.[8]

It will be recalled that the main purpose of this investigation was to determine the effect of the concentration of the indicator solution, and the current density, on the velocities of the boundaries, and the resulting effect on the computed mobilities and transference numbers. In Tables II to V are given the results of measurements on boundaries formed, in each case, with the solution being measured at 0.1 *N* and varying concentrations of the indicator solutions. Tables II and III are the results obtained on the movement of the boundary between potassium and lithium chlorides with two different potential gradients in the tube, and Tables IV and V are corresponding results for potassium bromide solutions. The figures given in Tables IV and V are averages, in each case, of closely agreeing duplicates, whereas the corresponding figures in Tables II and III represent single experiments.

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[7] Lewis, THIS JOURNAL, **32**, 862 (1910).

[8] Lewis' formula is: $N = N' - vc$, in which $N$ is the Hittorf transference number, $N'$ the uncorrected value from the moving boundary measurements, $v$ the volume change at the electrode due to the passage of a Faraday, and $c$ the concentration. The cathode reaction consists of (a) the formation of 1 equivalent of silver, (b) the formation of $N$ equivalents of potassium halide and (c) the disappearance of an equivalent of AgCl. For KCl the resulting volume changes are (a) 10.3 cc., (b) 13.5 cc. and (c) 25.7 cc., the term (b) being the partial molar volume of KCl in 0.1 *N* solution, computed in the usual way from density measurements, multiplied by 0.49. The net change of volume is therefore 0.002 liter and the correction term 0.0002. The corresponding terms for KBr are (a) 10.5, (b) 17.3 and (c) 29.7.

### TABLE II

### EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON MOVEMENT OF BOUNDARY, TENTH NORMAL POTASSIUM CHLORIDE AT 25°

Potential gradient in KCl solution, 4 volts per cm.

| Conc. indicator soln. (LiCl) | Velocity Cm. per sec. × $10^3$ | $10^6 U_K$ in 0.1 $N$ KCl | Transference number of K ion |
|---|---|---|---|
| 0.1 | 2.713 | (678) | (0.507) |
| .0887 | 2.663 | (666) | ( .498) |
| .08 | 2.654 | (664) | ( .496) |
| .075 | 2.641 | (660) | ( .494) |
| .07 | 2.633 | 658 | .492 |
| .065 | 2.631 | 658 | .492 |
| .06 | 2.637 | 659 | .493 |
| .055 | 2.658 | (665) | ( .497) |
| .045 | 2.622 | (656) | ( .490) |
| .035 | 2.615 | (654) | ( .489) |

### TABLE III

### EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON MOVEMENT OF BOUNDARY, TENTH NORMAL POTASSIUM CHLORIDE AT 25°

Potential gradient in KCl solution, 3.5 volts per cm.

| Conc. indicator soln. (LiCl) | Velocity Cm. per sec. × $10^3$ | $10^6 U_K$ in 0.1 $N$ KCl | Transference number of K ion |
|---|---|---|---|
| 0.1 | 2.373 | (678) | (0.507) |
| .0887 | 2.324 | (664) | ( .497) |
| .08 | 2.312 | (661) | ( .494) |
| .075 | 2.309 | (660) | ( .493) |
| .07 | 2.303 | 657 | .492 |
| .065 | 2.298 | 656 | .491 |
| .06 | 2.296 | 656 | .491 |
| .055 | 2.309 | (660) | ( .493) |
| .035 | 2.287 | (653) | ( .489) |

### TABLE IV

### EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON MOVEMENT OF BOUNDARY, TENTH NORMAL POTASSIUM BROMIDE AT 25°

Potential gradient in KBr solution, 3.365 volts per cm.

| Conc. indicator soln. (LiBr) | Velocity Cm. per sec. × $10^3$ | $10^6 U_K$ in 0.1 $N$ KBr | Transference number of K ion |
|---|---|---|---|
| 0.1 | 2.557 | (764) | (0.564) |
| .09 | 2.373 | (709) | ( .523) |
| .08 | 2.247 | (671) | ( .495) |
| .075 | 2.223 | (664) | ( .490) |
| .07 | 2.202 | 657 | .485 |
| .065 | 2.201 | 657 | .485 |
| .06 | 2.272 | (680) | ( .501) |
| .05 | 2.275 | (679) | ( .501) |

Fig. 3 is a typical diagram which represents the data given in the tables. The mobilities computed from the experiments are plotted as ordinates against the corresponding concentrations of indicator solution. A similar plot is obtained if the transference numbers are used instead of the mobilities. The heavy line represents the values obtained at the higher potential gradient used and the lighter line those for a lower gradient. It will be seen from this plot, and also from the tables, that the velocity of the boundary (and therefore the computed mobilities and transference numbers) varies widely with the concentration of the following, or indicator, solution. However, at 0.065 $N$ for potassium chloride and at about the same concentration for potassium bromide there is a minimum in the curves. Within the experimental error the measured mobility at this point is unaffected by changing the potential gradient. In addition, at this point, the relation between the concentrations of the measured and indicator solutions corresponds closely to Equation 1

TABLE V

EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON MOVEMENT OF BOUNDARY, TENTH NORMAL POTASSIUM BROMIDE AT 25°

Potential gradient in KBr solution, 3.701 volts per cm.

| Conc. indicator soln. (LiBr) | Velocity Cm. per sec. × $10^3$ | $10^6$ $U_K$ in 0.1 $N$ KBr | Transference number of K ion |
|---|---|---|---|
| 0.08 | 2.465 | (669) | (0.494) |
| .075 | 2.427 | 659 | .486 |
| .07 | 2.423 | 658 | .486 |
| .065 | 2.416 | 656 | .484 |
| .06 | 2.498 | (678) | ( .501) |
| .05 | 2.497 | (678) | ( .501) |

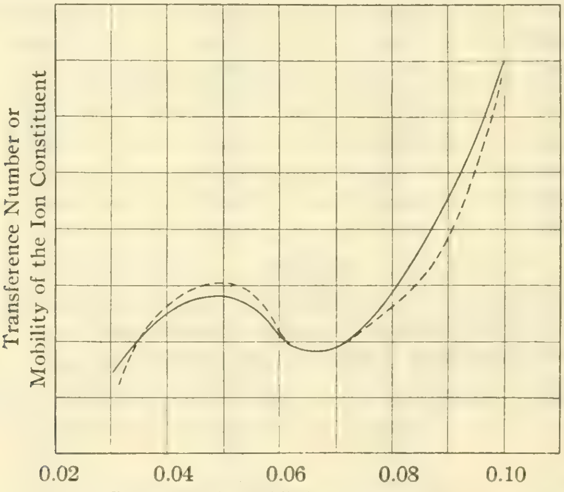

Fig. 3

$$C/T = C'/T'$$

For lithium chloride, for instance, the value for $T'$ computed from Equation 1 is 0.320 whereas the results of MacInnes and Beattie[9] give by interpolation the value of 0.316 for this concentration. The agreement would be exact if the minimum were taken as 0.064 *N*. In addition it will be seen, from an examination of the tabulated data, that on either side of the minimum there is a range of concentrations of indicator solution (about 5%) in which the measured mobilities and transference numbers are independent of this concentration within the experimental error. Apparently throughout this small range the automatic adjustment of the concentration of the indicator solution, as predicted by Kohlrausch, does take place. Outside this range the adjustment quite as evidently fails to occur. Erroneous values for transference numbers will therefore be obtained if the concentration of the indicator solutions is not adjusted within this range.

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[9] MacInnes and Beattie, THIS JOURNAL, **42**, 1117 (1920).

Some results have also been obtained which show that if the composition of the indicator solution is adjusted according to Equation 1, the transference number obtained by observation of the moving boundary is, within the experimental error, independent of the potential gradient. The figures are given in Table VI. The boundary becomes invisible, under the conditions of the experiments, with a potential gradient lower than about 2 volts per cm. If too large a potential gradient is used the boundary is distorted by heating effects.

Table VI

Results of Moving Boundary Experiments at Different Potential Gradients

Concentrations, KCl = 0.1 *N*; LiCl = 0.065 *N*

| Current Amp. × $10^3$ | Gradient (volts/cm.) in KCl solution | $10^6 U_K$ | Transference number of potassium ion |
|---|---|---|---|
| 5.893 | 4 | 658 | 0.492 |
| 5.156 | 3.5 | 657 | .491 |
| 4.420 | 3 | 656 | .491 |
| 4.051 | 2.75 | 660 | .494 |
| 3.683 | 2.5 | 657 | .492 |
| 3.315 | 2.25 | 657 | .492 |
| 2.951 | 2 | No boundary visible | |

In practical use of the moving boundary method for determining transference numbers an estimate of the probable value of the number should be made and the indicator solution concentration should then be computed according to Equation 1, and a measurement made. The indicator concentration should then be varied slightly and the measurement repeated. This should be continued until a portion of a plot similar to Fig. 3, and including the minimum value, can be prepared.

Further, the value obtained should be shown to be independent of the current through the apparatus, that is, to the potential gradients in the solutions. This procedure may sound tedious, but it is far more rapid, and also more accurate, than the determination of the same numbers by the Hittorf method. It also appears desirable that evidence showing that the adjustment of the compositions of the measured solution and the indicator solution has been obtained, should be given in all future work with the moving boundary method.

It does not, at present, appear to be possible to give a clear picture as to why the boundaries move too fast on both sides of the "adjustment" represented by Equation 1, and why, on the side of a too dilute indicator solution, the apparent mobility passes through a maximum and then again decreases. Some experiments under consideration will, we hope, throw light on the subject. It seems probable, however, that if the adjustment to the conditions of Equation 1 cannot take place by the dilution of the indicator solution, the adjustment may occur in the leading solution.

## The Transference Numbers

In this investigation we have obtained accurate transference numbers for potassium chloride and potassium bromide solutions at 0.1 $N$ and at 25°. The value for potassium chloride, 0.492 ± 0.001, agrees substantially with the value, 0.493, given, by Denison and Steele. It is, however, somewhat lower than the number given by the Hittorf and e.m.f. methods, which average about 0.496.

Our transference number for potassium in potassium bromide, 0.485, lies between the value, 0.480, obtained by Denison and Steele by the moving boundary method, and the number, 0.495, found by Jahn and Bogdan[10] at 18°, and the same value obtained at 25° by Pierce and Hart[11] in an extensive investigation by the electromotive-force method.

This investigation was originally undertaken to obtain data for a further test of the relation

$$T \Lambda \eta^{n} = K \qquad (6)$$

in which $T$ is the transference number, $\Lambda$ the equivalent conductance, $\eta$ the relative viscosity, and the exponent $n$ an empirical constant. For the series of alkali chlorides and hydrochloric acid $K$ has been found, by one of the authors,[12] to be a constant at any one concentration. Physically, $K$ is the conductance of the ion in a solution whose relative viscosity is unity. Table VII gives the data and the computation for the potassium ion from the two salts at 0.1 $N$ and 25°. The effect of the viscosity is small,

Table VII

Conductance of Potassium Ion and the Influence of Viscosity

| | $\Lambda$ | $T_K$ | $\eta$ | $T_K\Lambda$ | $T_K\Lambda\eta$ |
|---|---|---|---|---|---|
| KCl | 128.99 | 0.492 | 0.9982 | 63.5 | 63.4 |
| KBr | 131.6[13] | .485 | .9946 | 63.8 | 63.5 |

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[10] Jahn and Bogdan, *Z. physik. Chem.*, **37,** 681 (1901).

[11] Pierce and Hart, This Journal, **43,** 2483 (1921).

[12] MacInnes, *ibid.*, **43,** 1217 (1921).

[13] Value determined by Stearn, *ibid.*, **44,** 674 (1922), multiplied by 128.99/128.34, the ratio of Stearn's value of $\Lambda$ for KCl to that recently determined by Kraus, *ibid.*, **44,** 2422 (1922).

but noticeable, at this low concentration. The exponent, *n*, has been assumed provisionally to be unity. It appears then, for this limited amount of data at least, that within the limit of error Equation 6 holds for the potassium ion as well as for the chloride ion. It is hoped to extend this investigation to cover a wide range of strong electrolytes.

## Summary

A modification of the moving boundary method of Denison and Steele for determining transference numbers, involving a single boundary, has been developed.

The boundaries move with the theoretical velocities only when the two solutions in contact at a boundary are adjusted, within about 5%, to the relation $C/T = C'/T'$ in which $C$ and $C'$ are the concentrations and $T$ and $T'$ are the transference numbers. The correct value for $T$ can therefore be obtained by a series of experiments approaching more and more closely to this condition. Unless this adjustment is obtained results are not independent of the composition of the indicator solution, or of the current through the apparatus, and may vary widely and erratically from the true values.

Transference numbers at 25°, for potassium chloride and potassium bromide in 0.1 $N$ solutions have been obtained. These numbers show that the conductance of the potassium ion is the same in these two solutions if correction is made for viscosity.

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# THE EQUATION OF STATE FOR PURE NITROGEN, GAS PHASE

by

Leighton B. Smith and Robert S. Taylor

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# THE EQUATION OF STATE FOR PURE NITROGEN, GAS PHASE[1]

By Leighton B. Smith and Robert S. Taylor

Received June 25, 1923

Following the method of Keyes, pure nitrogen has been investigated by the isometric method. The theoretical work in connection with the equation of state[2,3,4,5] has made it appear highly probable that in the case of a fluid composed of molecules of invariable type, the pressure should vary linearly with the temperature at constant volume. The truth of this proposition involves the consequence that the potential energy of any given species of molecule or atom should be a function of the volume only. The derivative of the potential energy or the cohesive pressure, as it has come to be designated, may be directly evaluated for each constant volume setting employed in the isometric method. The form of function which represents the cohesive pressure as well as the volume correction term is known and indeed the constants of the equation of state may be easily evaluated directly from the isometric data.

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[1] This investigation was undertaken by the Research Laboratory of Physical Chemistry at the request of the Bureau of Mines, working in coöperation with the War and Navy Departments. The Bureau of Mines as well as the Massachusetts Institute of Technology contributed liberally in funds needed to carry forward the work.

The present paper is the fourth published by this Laboratory presenting data required in perfecting the processes for the extraction of helium from natural gas.

[2] Phillips, (a) *J. Math. Phys., Mass. Inst. Techn.*, **1**, 42 (1921); (b) *Proc. Nat. Acad. Sci.*, **7**, 172 (1921).

[3] Keyes, This Journal, **43**, 1452 (1921).

[4] Keyes, *J. Math. Phys., Mass. Inst. Techn.*, **1**, 89 (1922).

[5] Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

The constants for the equation of state for atmospheric nitrogen based on the data of Amagat have been published by Keyes. Sufficient data, however, for pure nitrogen are not available and the purpose of the present work is to provide accurate data from which the fundamental constants for nitrogen may be deduced. Certain improvements in method and a greater accuracy in the volume control of the apparatus have been attained as a consequence of this study.

## Preparation of Pure Nitrogen

The nitrogen was prepared by heating a mixture of ammonium sulfate and potassium nitrite in solution.

Fig. 1 illustrates the apparatus employed for generating and purifying the gas. The flask A was partially filled with a concentrated solution of ammonium sulfate and a solution of potassium nitrite was introduced from the separatory funnel, drop by drop. A safety tube and manometer B served to indicate the pressure and to relieve it, if it became excessive. The evolution of nitrogen was readily controlled by the heating and the rate at which the solution was admitted.

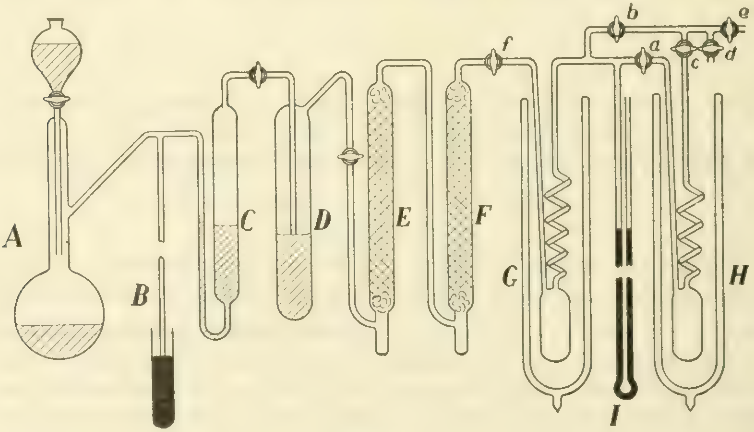

Fig. 1

The gas first passed through concd. sulfuric acid in the wash bottle C, then through a 20% solution of potassium hydroxide in D. E and F contained solid potassium hydroxide and phosphorus pentoxide, respectively. The gas was next passed through the bulb and spiral G immersed in liquid air which served to freeze and thus remove a large proportion of the impurities. From G the nitrogen passed to a similar arrangement at H which was immersed in liquid air through which hydrogen was bubbled. This so lowered the temperature of the liquid air that the nitrogen condensed to a liquid under a pressure of slightly more than 1 atmosphere. When a sufficient quantity of nitrogen had condensed in the bulb at H (about 20 cc.) the stopcocks a and f were closed and b and d opened, connecting G with the vacuum pump. G was now allowed to warm and the impurities that had condensed there were pumped away. The cock b was now closed and a opened for a short time, thus causing a portion of the liquid nitrogen to boil off and sweep out any fixed gaseous impurities in the vapor at H. The bulb and spiral at G were again cooled with liquid air through which hydrogen was then bubbled. The cock a was again opened and the bubbling of hydrogen at H stopped. As the temperature at H increased to that of liquid air boiling under 1 atmosphere pressure, the nitrogen slowly distilled from H and condensed at G. This process was stopped before all the liquid at H had disappeared and a was closed and C opened so that the residual nitrogen together with the impurities remaining in it were removed by the pump. This process of fractional distillation between G and H was repeated 5 times, and in each case the first and last fractions of distillate were discarded. The resulting liquid nitrogen was water-white and entirely free from particles of solid impurities. Finally, connection was made to the 6-liter Pyrex globe, which had previously been highly evacuated, and the nitrogen allowed to vaporize and fill the globe to somewhat over 1 atmosphere pressure.

## The Pressure Gage

The gage was that employed by Keyes, Smith and Joubert[6] in the work on the equation of state for methane gas phase and was of about 1 cm. in diameter.

It was calibrated against an open top mercury column about 9 meters high. A platinum needle in the short arm of the column for electrical contact with the surface of the mercury was used for detecting the equilibrium of the column. Temperature control of the column was obtained by enclosing it in a channel-shaped support closed on the front side by adjustable pieces of cardboard. The electrical system for detecting equilibrium of the gage consisted of a telephone with an audion bulb in circuit as indicated in Fig. 2. This device made possible the use of very feeble currents in the contact circuit, thus avoiding emulsification of the oil at the surface of the mercury and so insuring very sharp make and break. This emulsification of the mercury and oil is of very great importance in the compressibility measurements as it amounts to removing a small quantity of mercury from the piezometer portion of the system and thus changing its volume.

The length of the mercury column was measured on a steel tape, stretched by a load of 7 kg., which had been calibrated under the same stretching load by comparison with a standard meter compared at the United States Bureau of Standards. The complete data for the calibration of the gage have been published in the paper of Keyes, Smith and Joubert. The mean value of the constant is 1.0255 mm./g.

## The Compressibility Apparatus and Method of Loading the Piezometer

The general apparatus is shown in Fig. 2, which is a further development of the apparatus used by Keyes and Felsing.[7]

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[6] Keyes, Smith and Joubert, *J. Math. Phys., Mass. Inst. Techn.*, 1, 195 (1922).

[7] Keyes and Felsing, This Journal, 41, 589 (1919).

The floating pressure piston with scale pan and motor for oscillating the piston is represented at J, L and K. The oil injector I serves to adjust the height of the floating piston and to compensate for leak of oil around the floating piston. The steel block C contains a stopcock V for exhausting and an insulated needle D for indicating the mercury level. This contact serves to detect equilibrium of the load on the piston and the pressure exerted by the material in the piezometer. For example, if too great a weight is on the piston the mercury will be depressed, and if too small a weight it will rise and make contact; 1 g. suffices, as a rule, to make or break the contact. A shut-off is provided for closing the piezometer B from the entire apparatus while connection is made from the block C to the mercury volume-displacement piston apparatus G submerged in a constant temperature bath F, whose contents are stirred by means of the motor and propeller apparatus Q. The nut H serves to force the piston into the mercury, driving it through fine steel tubing of small bore into the piezometer. The advance of the piston is indicated by 100 divisions engraved on the under portion of the nut. Whole turns are counted by a "cyclometer" not shown in the drawing. It is possible with the 16mm. piston driven by a screw with 7.1 threads per cm. to estimate 0.001 turn of the nut, corresponding to about 0.00028 cc. The packing of the piston which moves into the cylinder G consists of cotton fabric heated in ceresin wax to 160°, and hard rubber forced into place by means of a steel ring driven by a screw cap.[8] The packing is perfectly tight over long

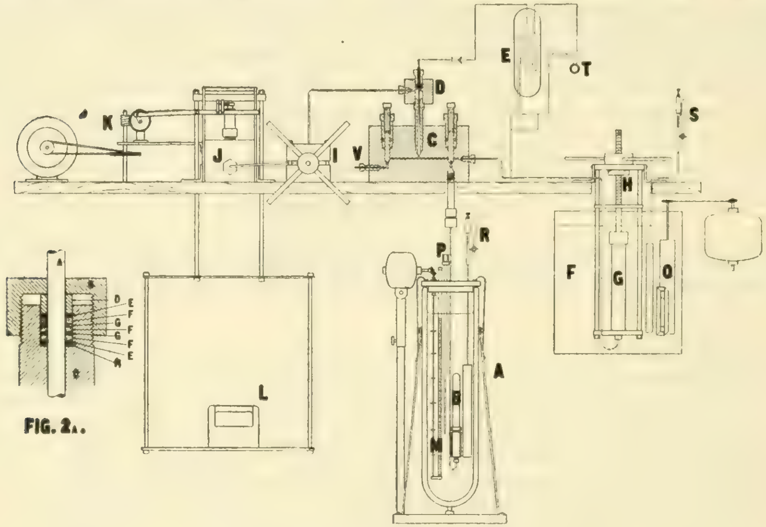

FIG. 2A.

Fig. 2

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[8] The diagram, Fig. 2A, shows the method of applying the packing to the piston in the mercury volume injector. The piston is represented by A and the nut driving the packing at B through pressure on the steel ring D. At the bottom of the packing gland is a steel ring H which also is a snug fit to the piston. E, E indicate hard rubber rings and F,F,F the cotton fabric (such as unbleached cotton) impregnated quickly with ceresin wax at 160°. G,G are rings of soft steel. The annular width of the packing gland is about 3 mm. and the depth for moderate pressures (500 atm.) about 3 to 4 cm. The hard rubber ring protects the waxed packing from the kerosene of the bath and serves to wipe the piston as it moves backward and forward, thus minimizing the removal of wax. This latter objective is not as satisfactorily accomplished as desirable, but no better method of wiping the piston has been applied.

periods of use after having been seasoned by exposing it to several hundred atmospheres with successive tightenings of the driving nut. A similar packing is used on the stopcocks of the block C.

The constant temperature bath represented at A, Fig. 2, consists of a Pyrex Dewar tube 6.6 cm. in inside diameter and 40 cm. in length. The disposition of the platinum thermometer, stirrer, heater and mercury in the steel regulator is evident from the figure. For the bath fluid a high-boiling light oil sufficed for the range 50° to 200°, while an ice-bath served to maintain the piezometer at 0°. The cover of the bath is of asbestos wood and carries the bearing for the stirrer and binding posts for the electrical connections of the heater. The Dewar tube bath here represented is very convenient and has been employed to 330°. It possesses obvious advantages due to its permitting a view of the interior at all times, and the heat insulation is excellent. The Dewar tube, however, requires prolonged heating at 450° during exhaustion. Recent tubes silvered in such a manner as to leave a clear strip 2 cm. to 5 cm. in width parallel to the long axis have greater heat-insulating properties, at the same time permitting a view of the interior. The silver will not peel, once it has been slowly and thoroughly baked out during exhaustion.

The piezometer is represented in detail at A, Fig. 3. It was made in one piece from cold rolled steel, the lower end being spun shut and welded with the oxy-acetylene flame.

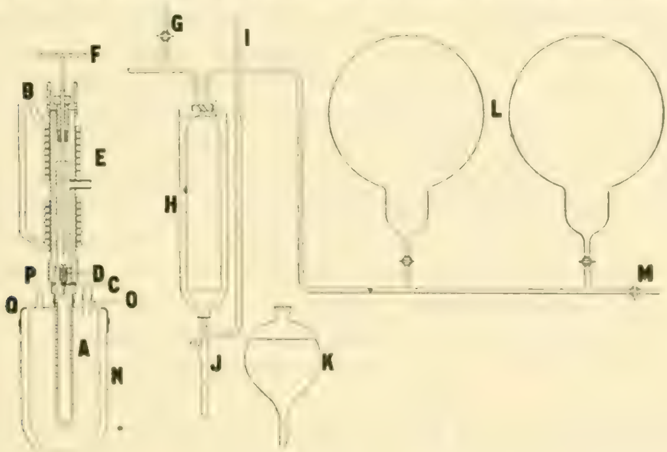

Fig. 3

A left hand thread was cut on the outer portion, where it screwed into the top piece E surrounded by a cooling coil of copper B. The latter piece carried a screw driver F passing through a packing gland and sealed with mercury. The piezometer was locked by means of the plug D, which had a 0.75 mm. hole drilled throughout its length. The locking of the piezometer was secured by the compression of the gold washer C against a seat in the piezometer by means of the screw D. The purpose of the cooling coil about E was to preserve the packing gland during the exhaustion of the bomb at 350°.

Nitrogen is, of course, above its critical temperature at ordinary temperatures, and it was necessary to place in the piezometer sufficient nitrogen to give a range of volumes per gram from 5 to 23 cc. over the temperature range 0° to 200°. The capacity of the piezometer was 13.3143 cc. at 0° to the under surface of the gold disk. The quantity of nitrogen employed was about 0.51 g., corresponding to about 410 cc. at N.T.P. and producing about 40 atmospheres pressure in the piezometer at ordinary temperatures.

The procedure of loading consisted in first exhausting the buret H connected by means of the 2-way stopcock with the piezometer, the latter being, of course, heated to drive off adsorbed matter. Nitrogen was then permitted to expand into H from the holders L and, when temperature equilibrium had been established, the pressure was read on the mercury column I. The buret was of the constant volume type, with the lower buret mark engraved on a tube of the same diameter as the manometric tube, thereby avoiding corrections for capillary depression. The nitrogen in the buret was transferred to the piezometer by cooling the latter in liquid air and raising the mercury reservoir K, thus liquefying the nitrogen in the piezometer. The vapor pressure of nitrogen at the temperature of liquid air is rather high, so the air was boiled under reduced pressure. For this purpose the Dewar tube containing the liquid air was provided with a spun cap of german silver Q that had an opening for the piezometer and tubes O and P for introducing liquid air and for connection with the vacuum pump. O could be closed with a rubber stopper. The cap was made fast to the Dewar tube and the piezometer by means of soft rubber tape and rubber cement. The air was boiled under a vacuum of 5 or 6 mm. of mercury which made it possible to liquefy the nitrogen under a pressure of 20 or 30 cm. The piezometer was then locked by screwing down the screw D by means of the screw driver F. The nitrogen remaining in the leads and in E above the gold disk was removed by means of a Toepler pump and the volume measured at a known temperature and pressure. To obtain the true mass requires the equation of state for nitrogen, or it suffices for the accuracy obtainable[9] to employ the weight of a liter at N.T.P.

The weight of a liter of pure nitrogen was taken as 1.2507 g., or the volume of a gram is 799.55 cc. as given by Moles.[10] Holborn and Otto[11] found for their nitrogen 1.2509 g., in fairly good agreement with the above. Later in this paper further reference to the matter of the weight of a liter of pure nitrogen will be made.

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[9] The gas is measured in the buret H, Fig. 3, under other conditions of temperature and pressure than N.T.P., under which the liter is measured. Strictly, one should know the compressibility and coefficient of expansion of the gas to obtain the true weight of the quantity actually measured. The use of the perfect-gas laws with the measured weight per liter leads to no appreciable error, however, in the case of nitrogen, as was proved when the constants of the equation of state were obtained. It will be shown in the present paper that the weight of a liter of nitrogen calculated by the equation of state agrees very well with the experimental determination of Moles.

[10] Moles, *J. chim. phys.*, **19**, 283 (1922).

[11] Holborn and Otto, *Z. Physik*, **10**, 367 (1922).

The loaded piezometer is connected with a piece of hexagonal steel carrying a steel tubing of 0.75 mm. bore locking against an annealed aluminum washer, and placed inverted in the constant-temperature bath. Referring again to Fig. 2, the piezometer with its steel tube may then be connected with the block C and the steel lead exhausted through V to the gold washer serving to confine the nitrogen in the piezometer. After closing the stopcock in block C at V, mercury may be run in by screwing in the piston of the mercury volume-injector G. It is to be added that a plug replaced the oil lead from I in D during the exhaustion and the oil lead was replaced after filling the block and lead with mercury. The oil lead having been connected, mercury is brought to the needle point by manipulating the oil injector I and volume injector G. By this means a zero setting may be obtained at a definite pressure corresponding to the position of the mercury which is in contact with the gold disk closing the piezometer. After the zero setting is obtained the pressure is increased to several hundred atmospheres and in about 24 hours the gold disk, weakened by amalgamation with the mercury, is punctured, bringing the mercury into contact with the nitrogen. By means of the mercury injector G a setting may be made for a chosen specific volume of nitrogen and a series of pressures and temperatures observed.

It is necessary to know expansion of the mercury with the temperature as well as its compressibility[12] while the stretch of the steel piezometer and apparatus may be obtained by separate blank measurements. For the true expansivity with temperature of the steel piezometer, the data of the Reichsanstalt were correlated as a function of the temperature as follows.

$$V_t^{Fe} = V_0 (1 + 3.25 \times 10^{-5} t + 2.85 \times 10^{-8} t^2 - 1.65 \times 10^{-11} t^3)$$

The equation for the volume of mercury as a function of the temperature, as given by Callendar and Moss, was employed.

$$V_t^{Hg} = V_0 (1 + 1.80555 \times 10^{-4} t + 1.2444 \times 10^{-8} t^2 + 2.539 \times 10^{-11} t^3)$$

The shifting of the temperature requires, for preserving constancy of the nitrogen volume, a resetting of the mercury injector G to compensate for the combined increase in volume of the mercury in the piezometer and the dilation of the piezometer with temperature and pressure. The method of making this computation is obvious, when the stretch of the piezometer and apparatus with pressure and the expansion of the piezometer and mercury with temperature are known.

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[12] The compressibility of mercury is a function of both pressure and temperature. Thus Bridgman gives the compressibility at 1 atmosphere as $3.80 \times 10^{-6}$ at 0° and $3.95 \times 10^{-6}$ at 22°. The decrease of the compressibility with pressure is given as about 3% for the first thousand atmospheres. The effect of increase in pressure may be neglected in the present work since 400 atmospheres was not exceeded. The temperature effect on the stretch of the piezometer is determined as the sum of that due to the compressibility of the mercury contained in the piezometer and the stretch of the piezometer itself. These direct measurements failed to disclose any pronounced effect on the combined mercury compressibility and piezometer stretch because of the small amount of mercury (13.3 cc.) contained in the piezometer and the smallness of the temperature coefficient of stretch of the piezometer. The value $3.9 \times 10^{-6}$ was assumed for the mercury compressibility independent of the temperature. The total stretch of the piezometer amounted to $9.73 \times 10^{-6}$ cc. per atm.

## The Experimental Data

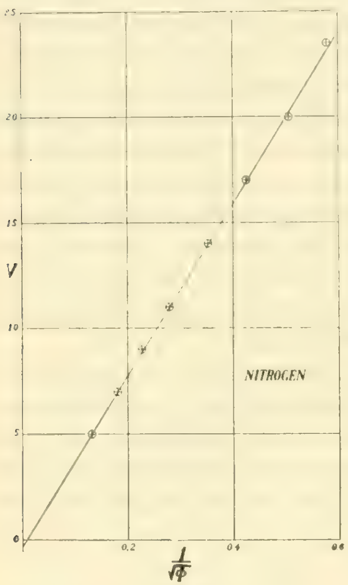

Fig. 4

The data were taken first at 50°, continued to 100°, 150° and 200°, and the observations at 0° were made last, using a Dewar tube filled with ice. In Table I will be found the absolute temperatures and pressures for the fixed volumes beginning with 23 cc. per g. of nitrogen. A linear equation is given with each volume which has been used to calculate the pressures recorded under each observed pressure.

The equation of state gives, for the tangent of the pressure-temperature lines at constant volume, the expression $R/(v - \delta)$. The magnitude of $R$ per mole is known with tolerable accuracy,[13] being 82.058 cc., atm. per degree C., per mole. The molecular weight of nitrogen has been taken as 28.02. The value of $R$ per g. of nitrogen is, therefore, 2.92855.

From the equations for the isometrics the constants for the cohesive pressure term $\Phi = A/(v - l)^2$ may be derived. The constant of the linear equation for each volume is equal to $\Phi$ for that volume. These values were calculated over to $1/\sqrt{\Phi}$ and plotted against $v$ giving a straight line as shown in Fig. 4. When we represent this by an equation of the form $V = a + \frac{b}{\sqrt{\Phi}}$, we see

TABLE I

OBSERVED PRESSURE REPRESENTED AS A LINEAR FUNCTION OF THE TEMPERATURE AT CONSTANT VOLUME

| Volume Cc. | 0° | 49.98° | 100° | 152.34° | 200° | Pressure |
|---|---|---|---|---|---|---|
| | | | $p = 0.136096T - 2.9794$ | | | |
| 23 | 34.175 | 41.012 | 47.812 | 54.930 | 61.380 | Obs. |
| | 34.193 | 40.896 | 47.804 | 54.927 | 61.413 | Calc. |
| | | | $p = 0.157963T - 3.8947$ | | | |
| 20 | 39.251 | 47.141 | 55.088 | 63.322 | 70.839 | Obs. |
| | 39.251 | 47.146 | 55.048 | 63.315 | 70.844 | Calc. |

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[13] Keyes, *J. Am. Soc. Refrig. Eng.*, **8,** 505 (1922).

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | $p = 0.188830T-5.5225$ | | | |
| 17 | 46.054 | 55.503 | 65.021 | 74.809 | 83.766 | Obs. |
| | 46.054 | 55.492 | 64.938 | 74.821 | 83.821 | Calc. |
| | | | $p = 0.233740T-8.0190$ | | | |
| 14 | 55.835 | 67.470 | 79.281 | 91.443 | 102.545 | Obs. |
| | 55.824 | 67.507 | 79.199 | 91.433 | 102.573 | Calc. |
| | | | $p = 0.306481T-12.7333$ | | | |
| 11 | 70.979 | 86.290 | 101.698 | 117.676 | 132.197 | Obs. |
| | 70.977 | 86.297 | 101.627 | 117.668 | 132.275 | Calc. |
| | | | $p = 0.388372T-19.3732$ | | | |
| 9 | 86.707 | 106.130 | 125.564 | 145.765 | 163.911 | Obs. |
| | 86.705 | 106.118 | 125.544 | 145.871 | 164.381 | Calc. |
| | | | $p = 0.521857T-30.4779$ | | | |
| 7 | 111.962 | 138.263 | 164.401 | 191.614 | 216.152 | Obs. |
| | 112.060 | 138.145 | 164.248 | 191.562 | 216.434 | Calc. |
| | | | $p = 0.798581T-57.9004$ | | | |
| 5 | 160.224 | 200.153 | 240.052 | 281.956 | 319.534 | Obs. |
| | 160.220 | 200.137 | 240.082 | 281.880 | 319.940 | Calc. |

that $l = -a$ and $A = b^2$. In Table II are listed the observed Φ's and those calculated from the equation $\Phi = \frac{1623.6}{(v + 0.2954)^2}$.

Table II

Cohesive Pressure Deduced from Intercepts of Straight-Line Equations Compared with Cohesive Pressure Calculated by Means of the Equations

$$\Phi = \frac{1623.6}{(v + 0.2954)^2} \text{ (Eq. a), and } \Phi = \frac{1623.3}{v^2} e^{-\frac{0.5732}{v}} \text{ (Eq. b)}$$

| Volume Cc. | Φ | Φ Calc. from Eq. a | Φ Calc. from Eq. b |
|---|---|---|---|
| 23 | 2.979 | 2.992 | 2.993 |
| 20 | 3.895 | 3.942 | 3.944 |
| 17 | 5.523 | 5.428 | 5.431 |
| 14 | 8.019 | 7.945 | 7.950 |
| 11 | 12.733 | 12.726 | 12.735 |
| 9 | 19.373 | 18.791 | 18.804 |
| 7 | 30.478 | 30.506 | 30.524 |
| 5 | 57.900 | 57.901 | 57.900 |

To complete the equation of state it remains to obtain the constants for the δ equation. δ was calculated for each observed pressure from the relation $\delta = v - \frac{RT}{p + \Phi}$. The values for each volume were averaged and the mean values log δ were plotted against $1/v$. The plot is reproduced in Fig. 5, showing that nitrogen follows the function $\delta = \beta e^{-\alpha/v}$.

The complete equation of state for nitrogen is, therefore,

$$p = \frac{2.92855}{v - \delta} T - \frac{1623.6}{(v + 0.2945)^2}, \quad \log_{10} \delta = 0.18683 - \frac{0.3113}{v} \qquad (1)$$

Table III

Values of $\delta$ for Individual Temperatures Calculated from Observed Pressures and the Value of $\Phi$ Given by the Equation $\Phi = \dfrac{1623.63}{(v + 0.2954)^2}$

| Volume Cc. | 0° | 49.98° | 100° | 152.34° | 200° | $\delta$ Mean | $\delta$ Calc. |
|---|---|---|---|---|---|---|---|
| 23 | 1.4781 | 1.4958 | 1.4908 | 1.4876 | 1.4749 | 1.4854 | 1.490 |
| 20 | 1.4807 | 1.4758 | 1.4881 | 1.4754 | 1.4711 | 1.4782 | 1.483 |
| 17 | 1.4624 | 1.4698 | 1.4886 | 1.4705 | 1.4652 | 1.4753 | 1.474 |
| 14 | 1.4584 | 1.4524 | 1.4721 | 1.4629 | 1.4594 | 1.4610 | 1.461 |
| 11 | 1.4438 | 1.4432 | 1.4499 | 1.4446 | 1.4324 | 1.4428 | 1.441 |
| 9 | 1.4178 | 1.4250 | 1.4301 | 1.4279 | 1.4160 | 1.4234 | 1.420 |
| 7 | 1.3854 | 1.3931 | 1.3934 | 1.3902 | 1.3824 | 1.3888 | 1.388 |
| 5 | 1.3328 | 1.3320 | 1.3324 | 1.3336 | 1.3289 | 1.3319 | 1.332 |

In Table IV will be found the pressures calculated by means of Equation 1 for comparison with the observed values.

Table IV

Nitrogen Isometrics

| Sp. vol. | | 0.0° 273.14° Press. atm. | 49.98° 323.12° Press. atm. | 100.00° 373.14° Press. atm. | 152.34° 425.48° Press. atm. | 200.00° 473.14° Press. atm. |
|---|---|---|---|---|---|---|
| 23 | Obs. | 34.175 | 41.012 | 47.812 | 54.930 | 61.380 |
| | Calc. | 34.196 | 41.000 | 47.810 | 54.936 | 61.425 |
| 20 | Obs. | 39.251 | 47.141 | 55.088 | 63.322 | 70.839 |
| | Calc. | 39.256 | 47.198 | 55.072 | 63.350 | 70.887 |
| 17 | Obs. | 46.054 | 55.503 | 65.021 | 74.809 | 83.766 |
| | Calc. | 46.092 | 55.520 | 64.955 | 74.827 | 83.817 |
| 14 | Obs. | 55.835 | 67.470 | 79.281 | 91.443 | 102.545 |
| | Calc. | 55.848 | 67.521 | 79.204 | 91.428 | 102.559 |
| 11 | Obs. | 70.979 | 86.290 | 101.698 | 117.676 | 132.197 |
| | Calc. | 70.955 | 86.267 | 101.591 | 117.626 | 132.228 |
| 9 | Obs. | 86.707 | 106.130 | 125.564 | 145.765 | 163.911 |
| | Calc. | 86.737 | 106.047 | 125.372 | 145.594 | 164.008 |
| 7 | Obs. | 111.962 | 138.263 | 164.401 | 191.614 | 216.152 |
| | Calc. | 112.029 | 138.110 | 164.212 | 191.525 | 216.396 |
| 5 | Obs. | 160.224 | 200.153 | 240.052 | 281.956 | 319.534 |
| | Calc. | 160.175 | 200.080 | 240.016 | 281.804 | 319.856 |

$$p = \frac{RT}{v - \delta} - \frac{1623.63}{(v + 0.2954)^2} \text{ where } \log \delta = 0.18683 - \frac{0.3113}{v}$$

$$R = 2.92855 \qquad \beta = 1.5376 \text{ and } \alpha = 0.7169$$

It seems probable that the true form of the cohesive-pressure equation is $\dfrac{A'}{v^2} e^{-l'/v}$ where $A'$ and $l'$ are constants of similar significance to the constants in the form $A/(v + l)^2$. In the gas phase it is difficult to distinguish between the two forms. Thus $\dfrac{A'}{v^2} e^{-l'/v}$ for large volumes becomes, with sufficient accuracy, equal to $\dfrac{A'}{v^2}\left(1 - \dfrac{l'}{v}\right) = \dfrac{A'}{v^2\left(1 + \dfrac{l'}{2v}\right)^2} \equiv \dfrac{A}{(v + l)^2}$.

Hence, for the gas phase $A = A'$ and $2l = l'$. In order to determine the constants of this exponential form, one takes logarithms of both sides,

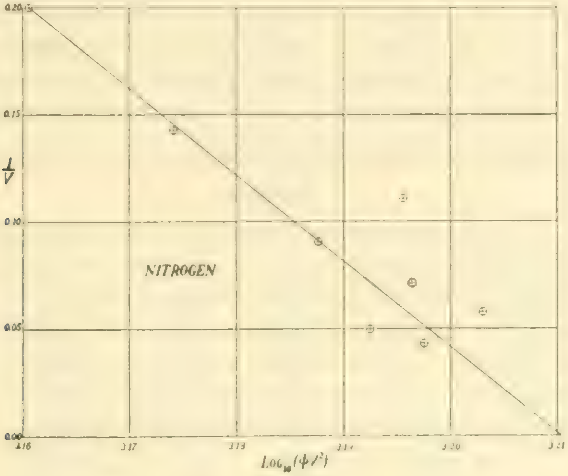

Fig. 4a

whence one gets $\log \Phi = \log \frac{A}{v^2} - \frac{l'}{v}\cdot$ Hence, a plot of $\log \Phi v^2$ against $1/v$ should give a straight line. Fig. 4a shows that a straight line is all that the assemblage of points will justify. Giving most weight to the high-pressure points, since they always serve to locate the constants better than low-pressure data, one obtains the following constants: $A = 1623.3$, and $l = 0.2866$. This is an excellent check and shows that the two forms are interchangeable as far as the present data go. The equation is $\log \Phi = \log \frac{1623.3}{v^2} - \frac{0.2489}{v}\cdot$ In Table II are also given the values of Φ calculated from this second form.

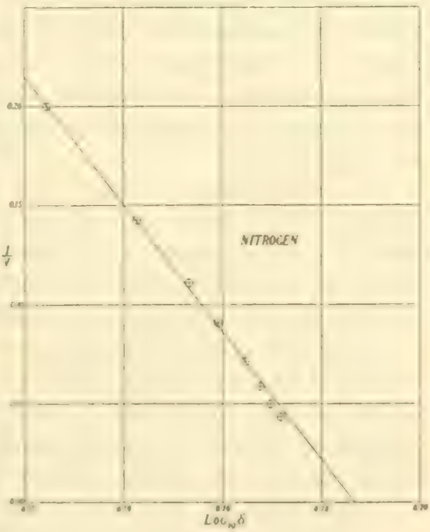

Fig. 5

## Weight of a Liter of Nitrogen at Normal Temperature and Pressure

Moles has most recently measured the normal density of nitrogen[10] obtaining 1.2506 g. per liter as the mean of four volumetric determinations in good agreement with the mean value

1.2507 of 29 determinations by four authors using two different experimental methods with nitrogen produced by eight different reactions. Holborn and Otto[11] as a test of the purity of their nitrogen determined the weight of a liter to be 1.2509 g. The equation of state gives 779.40 cc. as the volume of 1 g. at 0° and 1 atm. pressure. The reciprocal of this multiplied by 1000 gives 1.2509 as the weight of 1 liter at N.T.P.

## Equation of State for Atmospheric Nitrogen from Measurements by Amagat

Amagat[14] has measured the isotherms for gaseous atmospheric nitrogen. The data are divided into two series, the first set extending over a range of pressure from 100 to 1000 atmospheres and from 0.0° to 199.5°. The second series covers the range of pressures from 1000 to 3000 atmospheres and from 0.0° to 43.6°. The volumes given are relative to the capacity of a manometric tube and are not absolute. Keyes[15] has derived an equation from the low-pressure measurements which he gives as

$$p = \frac{2.9138}{v - \delta}T - \frac{1587.2}{(v - 0.007)^2}, \quad \log \delta = 0.2200 - \frac{0.284}{v}$$

He assumes the composition of atmospheric nitrogen to be 1.66% argon and 98.34% nitrogen by weight. The apparent molecular weight is taken as 28.163. The volume of 1 g. is taken as 795.12 cc.

Rayleigh,[16] Regnault, Von Jolly and Leduc have determined the weight of a liter of atmospheric nitrogen. Regnault's value was corrected by Crafts for contraction of the globe and Von Jolly's was corrected by Rayleigh. Rayleigh's and Leduc's values are the latest available and are in best agreement. The mean of their values, 1.25714 g., was assumed as the best figure for the weight of a liter. This gives 795.46 cc. as the volume of 1 g.

Two methods are available for determining the apparent molecular weight. From the weight of a liter of argon, 1.78094,[17] the weight of a liter of pure nitrogen[10] 1.2507 and the weight of a liter of atmospheric nitrogen, the composition of atmospheric nitrogen may be calculated. This method, which is not very accurate, gives 1.21% of argon.

Guye[18] gives the percentage by volume of oxygen in air as 20.94 and the weight of 1 liter of air as 1.2928 g. Keyes[13] gives 699.77 cc. as the best value for the volume of 1 g. of oxygen. Therefore, we obtain 23.147% oxygen by weight. Moureu and Lepape[19] give the percentage of argon in air as 1.29 by weight. From this, the composition of atmospheric nitrogen is 1.679% argon and 98.321% nitrogen by weight. This gives for the apparent molecular weight $\dfrac{1}{\dfrac{0.01679}{39.88}+\dfrac{0.98321}{28.020}} = 28.161$ using the accepted values of 39.88 and 28.020 for the molecular weights of argon and pure nitrogen. The gas constant $R$ per gram is, therefore, 82.058/28.161 = 2.9139, which coincides with that obtained by Keyes.

---

[14] Amagat, *Ann. chim. phys.*, **29**, 68 (1893).

[15] Keyes, THIS JOURNAL, **42**, 54 (1920).

[16] Rayleigh, "Scientific Papers," Vol. **IV**, 51 (1893), or *Proc. Roy. Soc.*, **53**, 134 (1893).

[17] Watson, *J. Chem. Soc.*, **97**, 833 (1910).

[18] Guye, *J. chim. phys.*, [4] **15**, 570 (1917).

[19] Moureu and Lepape, *Ann. chim.*, [9] **4**, **5**, 4 (1915).

### Table V

### Amagat's High Pressure Isometrics

| Vol. actual cc./g. | Vol. A units | 0° Press. atm. | 16.0° Press. atm. | 43.6° Press. atm. | 16.0° Press. calc. from st. line eqs. | Eq. used |
|---|---|---|---|---|---|---|
| 1.647 | 0.00207 | 1000 | 1088 | 1239 | 1087.7 | 1 |
| 1.548 | .001946 | 1200 | 1298 | 1474 | 1300.6 | 2 |
| 1.443 | .0018135 | 1500 | 1613 | 1812 | 1614.5 | 3 |
| 1.364 | .0017145 | 1800 | 1937 | 2168 | 1935.0 | 4 |
| 1.323 | .0016635 | 2000 | 2150 | 2401 | 2147.2 | 5 |
| 1.260 | .0015835 | 2400 | 2572 | 2858 | 2568.1 | 6 |
| 1.213 | .0015250 | 2800 | 2990 | .. | .... | 7 |

1. $p = 5.482\ T - 497.36$
2. $p = 6.284\ T - 516.4$
3. $p = 7.156\ T - 454.6$
4. $p = 8.440\ T - 505.3$
5. $p = 9.197\ T - 512.1$
6. $p = 10.505\ T - 469.3$
7. $p = 11.875\ T - 443.5$

Amagat's series for 1000 to 3000 atmospheres extends over a very short temperature range. Table V gives his constant volume values and also the actual volumes in cc. per g. as obtained by multiplying his relative volumes by 795.5. Straight-line equations were passed through the points at 0.0° and 43.6° and are given below Table V. In Col. 6, Table V are given the pressures at 16.0° calculated from the corresponding constant-volume equations. These show that, within Amagat's limits of accuracy, $p$ is a linear function of $T$ at constant volume up to 3000 atmospheres.

In Fig. 6 the line represents the plot of log $\delta$, as calculated from Keyes' equation, against $1/v$. The points represent the observed values obtained from Amagat's high-pressure series. The fact that all of the observed points fall upon one side of the line indicates that Amagat's low-pressure series is not entirely concordant with his high-pressure series.

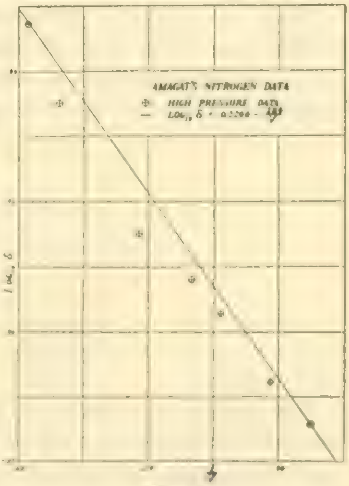

Fig. 6

### Comparison of the Recent Work of Holborn and Otto with the Equation of State for Nitrogen

Holborn and Otto[11] have recently measured the products of $p \times v$ for oxygen, nitrogen and helium. They represent their data by equations of the form $pv = f(p)$ and $pv = f\,1/v$. For the second form they give equations representing the 0°, 50° and 100° isotherms for nitrogen, which when converted to $v$ in cc. per g. and $p$ in atmospheres are as follows:

$$pv = (pv)_0 \left(1 - \frac{0.4563032}{v} + \frac{2.92858}{v^2}\right) \text{ at } 0.0° \qquad (2)$$

$$pv = (pv)_0 \left(1 - \frac{0.0262332}{v} + \frac{3.06343}{v^2}\right) \text{ at } 50.0° \qquad (3)$$

$$pv = (pv)_0 \left(1 + \frac{0.279970}{v} + \frac{3.18418}{v^2}\right) \text{ at } 100.0° \qquad (4)$$

From the equation of state,

$$pv = RT\frac{v}{v - \delta} - A\,\frac{v}{(v + l)^2}$$

Expanding this in the form of a series gives

$$pv = RT\,v\left(\frac{1}{v} + \frac{\delta}{v^2} + \frac{\delta^2}{v^3} + \frac{\delta^3}{v^4} + \ldots .\right) - Av\left(\frac{1}{v^2} - \frac{2l}{v^3} + \frac{3l^2}{v^4} \ldots\ldots\right)$$

but

$$\delta = \beta e^{-\alpha/v} = \beta\left(1 - \frac{\alpha}{v} + \frac{\alpha^2}{2v^2} - \frac{\alpha^3}{6v^3} + \ldots .\right)$$

Neglecting all terms of higher order than $1/v^2$ there is obtained

$$pv = RT\left[1 + \frac{1}{v}\left(\beta - \frac{A}{RT}\right) + \frac{1}{v^2}\left(\beta^2 - \alpha\beta + \frac{2Al}{RT}\right)\right] \qquad (5)$$

Since $(pv)_0 = RT$, Equation 5 is seen to be, at constant temperature, of the same form as Equations 2, 3 and 4. Substituting in (5) the constants of the equation of state for 0.0°, 50.0° and 100.0° one obtains the following equations for comparison with those of Holborn and Otto.

$$pv = (pv)_0 \left(1 - \frac{0.49227}{v} + \frac{2.45735}{v^2}\right) \text{ at } 0.0° \qquad (6)$$

$$(pv)_0 = RT = 799.890$$

$$pv = (pv)_0 \left(1 - \frac{0.17819}{v} + \frac{2.27236}{v^2}\right) \text{ at } 50.0° \qquad (7)$$

$$(pv)_0 = 946.317$$

$$pv = (pv)_0 \left(1 + \frac{0.05172}{v} + \frac{2.13694}{v^2}\right) \text{ at } 100.0° \qquad (8)$$

$$(pv)_0 = RT = 1092.745$$

For comparison purposes there are given in Table VI, values of pressures in atmospheres and corresponding volumes in cc. per g. at 0°, 50° and 100° from determinations by Holborn and Otto. These values for volume were converted from the arbitrary units by multiplying the latter by the factor 607.43 which is that given by the equation of state when $p$ = 1 meter = 1.31579 atm. and $T$ is 273.135 abs.

TABLE VI

PRESSURES AND VOLUMES COMPUTED FROM EQUATIONS BY HOLBORN AND OTTO

| Press. meters of Hg | Press. atm. | Volumes (cc. per g.) 0° | 50° | 100° |
|---|---|---|---|---|
| 10 | 13.158 | 60.449 | 71.930 | 83.266 |
| 30 | 39.474 | 19.993 | 24.022 | 27.951 |
| 50 | 65.789 | 11.943 | 14.477 | 16.920 |
| 70 | 92.105 | 8.532 | 10.418 | 12.214 |

From the equation of state pressures were calculated corresponding to the volumes given in Table VI.

These values are listed in Table VII.

TABLE VII

PRESSURES FROM EQUATION OF STATE USING VOLUMES AND TEMPERATURES FROM TABLE VI

| 0° | | 50° | | 100° | |
|---|---|---|---|---|---|
| $v$ | $p$ | $v$ | $p$ | $v$ | $p$ |
| 60.449 | 13.134 | 71.930 | 13.128 | 83.266 | 13.135 |
| 19.993 | 39.270 | 24.022 | 39.257 | 27.951 | 39.275 |
| 11.943 | 65.376 | 14.477 | 65.275 | 16.920 | 65.268 |
| 8.532 | 91.533 | 10.418 | 91.203 | 12.214 | 91.142 |

The pressures resulting from the present work corresponding to the volumes and temperatures given by Holborn and Otto are seen to be lower at about 90 atm. by 0.6%. It will be pointed out subsequently that until the "pure" nitrogen chemically prepared had been fractionated to remove traces of nitric oxide the higher pressures were obtained.

In Table VII of Holborn and Otto's paper are given values of the $pv$ product at 0°, 50° and 100° for various constant densities. The values of 5, 15, 25, 35, 45 and 55 in their arbitrary units were chosen. Multiplying the $pv$ products by the density gives the pressures in meters. Converting the densities to cc. per g. and the pressures to atmospheres, as explained above, the values contained in Table VIII were obtained.

TABLE VIII

PRESSURES AT CONSTANT VOLUME FROM HOLBORN AND OTTO

| $\frac{1}{v}$ (arb. units) | $v$ (cc. per g.) | Pressures (atm.) 0° | 50° | 100° |
|---|---|---|---|---|
| 5 | 121.486 | 6.564 | 7.789 | 9.010 |
| 15 | 40.495 | 19.596 | 23.383 | 27.149 |
| 25 | 24.297 | 32.535 | 39.025 | 45.493 |
| 35 | 17.355 | 45.416 | 54.760 | 64.096 |
| 45 | 13.498 | 58.261 | 70.639 | 83.021 |
| 55 | 11.044 | 71.105 | 86.727 | 102.303 |

The above values of pressure are plotted against the absolute temperature as shown in Fig. 7. These constant volume lines are straight to within what is believed to be the accuracy of Holborn and Otto's results.

From Equation 5 we see that the coefficient of $1/v$ in the $pv$ product equation is equal to $\beta - \frac{A}{RT}$. Taking the coefficients of $1/v$ in Equations 2, 3 and 4 of Holborn and Otto and solving simultaneously for $A$ we obtain the 3 values 2223.2, 2162.4 and 2197.5, of which the mean is 2194.4. Substituting this mean value of $A$ we obtain for $\beta$ the 3 values 2.287, 2.293 and 2.288, of which the mean is 2.289.

Holborn and Otto prepared nitrogen from sodium nitrite and purified it by passing it through alkaline pyrogallol and over glowing copper. It is known that alkaline pyrogallol is likely to introduce carbon monoxide and Smyth and Roberts[20] have shown that unless the temperature of the copper is kept below 600° the copper oxide will decompose and introduce oxygen. Also, copper will not reduce oxides of nitrogen unless the temperature is fairly high. The good agreement between the weight of a liter as determined by Holborn and Otto and the accepted value does not necessarily indicate great purity of the gas since, in the first place, the weight of a liter is very difficult to obtain and second, since the molecular weight of carbon monoxide is essentially the same as that of nitrogen and since nitric oxide has only a slightly greater molecular weight, the pressure of appreciable quantities of these gases would not greatly affect the weight of a liter, but would affect the magnitude of the $A$ and $\beta$ constants greatly. Previous to the work on the equation of state of pure nitrogen as given in this paper an equation was determined for a sample of gas purified by the

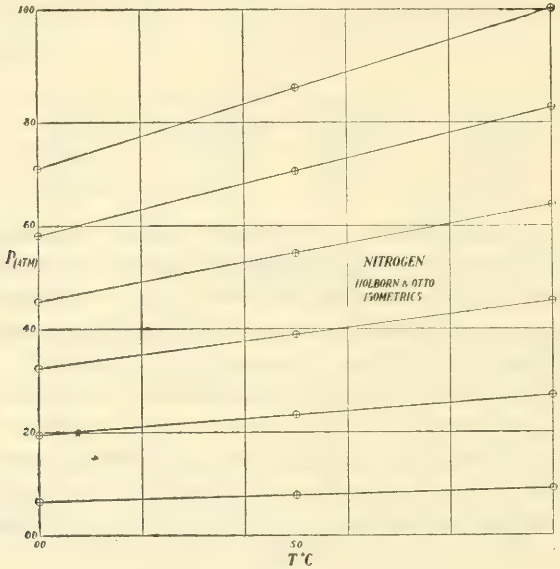

Fig. 7

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[20] Smyth and Roberts, THIS JOURNAL, **42**, 2582 (1920).

usual chemical methods. An $A$ constant of about 1860 was obtained, which lies much nearer the value obtained above from Holborn and Otto's work. Subsequently it was found that when this sample of nitrogen was condensed, suspended solid impurities were observed in the liquid. After 5 fractional distillations a perfectly water-white liquid was obtained that was undoubtedly pure. This procedure was used in preparing the gas for the measurements upon which the equation of state was based. Since the impurities mentioned as likely to be present in nitrogen, purified by chemical means, are all less perfect gases than nitrogen, their presence in small amounts would tend to increase the magnitude of the constants.

## Compressibility Coefficients

Maverick,[21] both alone and in collaboration with Batuecas, has made measurements on the compressibility coefficients at 1 atmosphere and 0°. Those made by Maverick alone seem to be more consistent than the others. His $\lambda$ is defined as equal to $-\frac{1}{(pv)_{760}}\left(\frac{\partial(pv)}{\partial p}\right)_T$.

His average value and those of other observers at 0° are Maverick, 0.00044; Chappuis,[22] 0.00043; Leduc and Sacerdote,[23] 0.00038; Rayleigh,[24] 0.00056. Maverick's values for nitrogen prepared from urea were discarded because of impurities in the gas so prepared.

From Equations 2, 3 and 4 of Holborn and Otto values of $\lambda$ are obtained as follows: 0°, 0.000561; 50°, 0.000023; 100°, —0.000360.

From Equations 6, 7 and 8 derived by the equation of state the following are obtained: 0°, 0.000608; 50°, 0.000216; 100°, —0.000071.

Owing to the extreme accuracy with which an observer must work in order to obtain any percentage accuracy for this coefficient, the agreement is about as good as can be expected. Keyes[4] has worked over the values for compressibility coefficients of Chappuis, Leduc and Sacerdote, and Rayleigh, comparing them with values obtained from the equation of state for atmospheric nitrogen.

In conclusion it is desired to thank Professor F. G. Keyes for his valuable suggestions and assistance, without which this work could not have been carried out.

## Summary

1. The $p$, $v$, $T$ relationship of pure gaseous nitrogen has been studied by the isometric method over the range of temperatures from 0° to 200° and 30 to 330 atmospheres' pressure. The Keyes equation represented

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[21] Maverick, *Thesis*, University of Geneva, No. 708, Jan., **1923** (to be published soon in *J. chim. phys.* and *Chim. Helvetica Acta*).

[22] Chappuis, *Trav. mem. bur. intern.*, **13**, 66 (1903).

[23] Leduc, *Ann. chim. phys.*, [7] **15** (1899); *Compt. rend.*, **123**, 743 (1896); **125**, 297 (1897); **148**, 407 (1909).

[24] Rayleigh, *Proc. Roy. Soc.*, **73**, 153 (1904); *Z. physik. Chem.*, **37**, 713 (1901).

the data within the experimental limits of error. This equation obtained is, $p_{\text{atm.}} = \dfrac{2.92855\,T}{v - \delta} - \dfrac{1623.63}{(v + 0.2954)^2}$ where $\log \delta = 0.18683 - \dfrac{0.3113}{v}$.

2. The weight of a liter of nitrogen at N.T.P. was calculated from the equation of state to be 1.2509 g. as compared with the generally accepted value of 1.2507 g.

3. The compressibility coefficient at 0° was calculated and found to be 0.00061 as compared with 0.00056 from Holborn and Otto's equation and the work of Rayleigh, and 0.00043 and 0.00044 from Chappuis and Maverick, respectively.

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# CORRECTION TO THE EQUATION OF STATE FOR NITROGEN

by

L. B. Smith and R. S. Taylor

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[Contribution from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology]

# CORRECTION TO THE EQUATION OF STATE FOR NITROGEN[1]

By L. B. Smith and R. S. Taylor

Received November 3, 1926 Published December 16, 1926

The recalculation of certain quantities from the equation of state for nitrogen has disclosed an error in determining the mass of nitrogen employed in the equation of state measurements. The mass of nitrogen actually present was 0.51185 g. instead of 0.51451 g. as originally computed.

The pressures and temperatures measured remain as given in the original article while the volumes are increased in the ratio of 0.51451 to 0.51185 (1.005197). The change in specific volumes modifies somewhat the constants of the equation of state for nitrogen. The equation as now determined is as follows: $p = [2.9286/(v - \delta)]\ T - 1650.5/(v + 0.313)^2$, where $\log_{10} \delta = 0.2174 - (0.4307/v)$, $\beta = 1.6497$ and $\alpha = 0.9918$. The pressures calculated from this equation are in substantially as good agreement with the observed pressures as those calculated from the old equation.

Van Urk[2] and more recently Verschoyle[3] have pointed out the fact that the $pv$ products for nitrogen at 0.0° as first reported are not in agreement with those of European observers.

Verschoyle, on the other hand, gives the following equation for his own 0.0° isotherm for nitrogen $pv = (1.00049 - 0.000496\ p + 0.000003334\ p^2)$, where pressures are in international atmospheres and volumes are referred to the volume of nitrogen at 0.0° and one atmosphere as unity. Verschoyle shows that this equation gives $pv$ values agreeing reasonably well with those of Holborn and Otto[4] and Van Urk

For purposes of comparison with our corrected $pv$ products, Verschoyle's equation has been converted to units of cc. per g. The weight of a liter of nitrogen at 0.0° and one atmosphere being taken as 1.2507 g., the volume of 1 g. becomes 799.55 cc. and the Verschoyle equation becomes $pv = 799.55\ (1.00049 - 0.0004961\ p + 0.000003334\ p^2)$.

Our observed $pv$ products and those calculated from the above equation of Verschoyle are listed in Table I.

Table I

Comparison of $pv$ Products at 0 0° Verschoyle and Smith and Taylor

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $p$, atm. | 34.175 | 39.251 | 46.054 | 55.835 | 70.979 | 86.707 | 111.962 | 160.224 |
| $pv$, obs | 790.10 | 789.09 | 786.98 | 785.74 | 784.81 | 784.41 | 787.80 | 805.29 |
| $pv$, calcd. | 789.50 | 788 48 | 787.32 | 786.66 | 785.22 | 785.59 | 788.95 | 804.82 |
| (Obs.-calcd.) | +0.60 | +0.61 | −0.34 | −0.92 | −0.41 | −1.18 | −1.15 | +0.47 |

---

[1] Smith and Taylor, "Equation of State for Pure Nitrogen, Gas Phase," This Journal, **45,** 2107 (1923).

[2] Van Urk, *Thesis*, Leiden, **1924.**

[3] Verschoyle, *Proc. Roy. Soc.*, **IIIA,** 552 (1926).

[4] Holborn and Otto, *Z. Physik,* **23,** 77 (1924).

The average deviation is seen to be a little less than one part in a thousand, which is somewhat better than the agreement between the values of Verschoyle, and Holborn and Otto, and Van Urk.

Verschoyle's inference that the gas used in our measurements was not pure is thus seen to be unfounded. In fact, the method of purification employed would preclude the possibility of "the presence of a gas of comparatively high boiling point."

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## THE TRANSFERENCE NUMBERS OF SOLUTIONS OF MIXED CHLORIDES. DISCUSSION OF PAPERS BY SCHNEIDER AND BRALEY AND BY BRALEY AND HALL

by

D. A. MacInnes

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# THE TRANSFERENCE NUMBERS OF SOLUTIONS OF MIXED CHLORIDES. DISCUSSION OF PAPERS BY SCHNEIDER AND BRALEY AND BY BRALEY AND HALL

BY D. A. MACINNES

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Schneider and Braley[1] have presented in THIS JOURNAL a paper on "The Transference Numbers of Sodium and Potassium in Mixed Chloride Solutions," in which they come to the conclusion that in a mixture of these salts there are ionic complexes of the type $K_x(NaCl_2)_y$. As evidence they present a large amount of data on the transference numbers of sodium and potassium ions in solutions of the mixed chlorides. It is clear that, if complexes of the type suggested are present, the transference numbers should vary in a different manner than would be expected if the solutions contain only simple ions. Further, they point out that proof of the presence of such complex ions in solution would be conclusive evidence against the possibility of complete dissociation of the solutions of strong electrolytes. Such proof would be, it may be added, equally effective evidence against the original ideas of Arrhenius. On account of the importance of the matter, it seems desirable to investigate the results of these authors carefully to see whether their conclusions are a necessary consequence of their experimental work.

In the first place, let us obtain an expression for the transference number of potassium ion in a mixture of sodium and potassium chlorides of total concentration $C$, in which $x$ is the ratio of the number of moles of potassium chloride in the solute to this total concentration. It will be assumed that the two salts are equally ionized, that no complexes are present, and that the mobility of each ion is constant at any given total salt concentration.[2] If $\Lambda_K$, $\Lambda_{Na}$ and $\Lambda_{Cl}$ are, respectively the ion conductances at the concentration $C$ of the ions represented by the subscripts, the transference number of the potassium ion in a mixture is given by the expression,

$$T_K = \frac{x\,C\,\Lambda_K}{C\,(x\,\Lambda_K + (1-x)\,\Lambda_{Na} + \Lambda_{Cl})} \qquad (1)$$

The numerator contains the conductivity contributed to the solution by the potassium ion, and the denominator the conduction by all the ions in the solution. At any total concentration $C$ the amount of chloride ion does not change with variations in the ratio $x$. The expression reduces to zero for $x = 0$ and to $T_K = \Lambda_K/\Lambda_{KCl}$ for $x = 1$. The similar expression for $T_{Na}$ need not be given.[3]

---

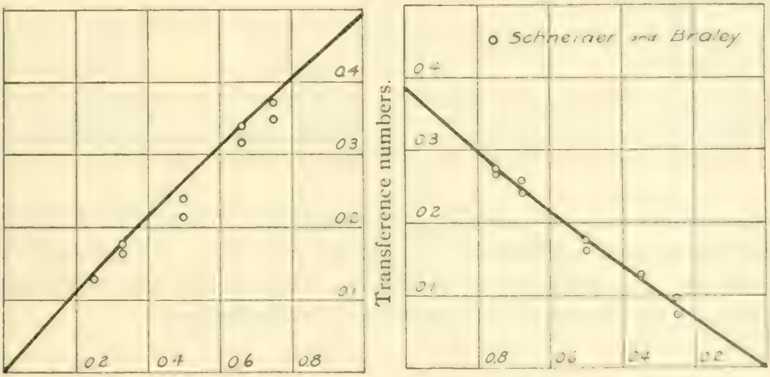
[1] Schneider and Braley, THIS JOURNAL, **45**, 1121 (1923).

[2] Evidence in favor of this latter assumption for solutions of the pure salts is given in a paper by the writer [MacInnes, *ibid.*, **43**, 1217 (1921)].

If $N_K$ and $N_{Na}$ are the transference numbers of the potassium and sodium ions in the solutions of the pure salts, and as, for these solutions, $(1 - N_K)\Lambda_{KCl} = (1 - N_{Na})\Lambda_{NaCl}$, the following expression may be readily obtained from Equation 1,

$$T_K = \frac{N_K\,(1 - N_{Na})}{(N_K - N_{Na}) + (1 - N_K)/x} \tag{2}$$

Thus the transference number $T_K$ in the mixture containing the proportion $x$ of potassium chloride may be found from a knowledge of the transference numbers of the two salts only. The assumptions involved in Equation 2 are, of course, the same as those for Equation 1.



Ratio—moles of KCl: total concn. Ratio—moles of NaCl: total concn.

Fig. 1.—0.1 *M*.

In Figs. 1, 2 and 3 Schneider and Braley's results are compared with the predictions of this simple theory, for the total concentrations 0.1, 0.2 and 0.4 *N*, respectively. In these diagrams the observed transference numbers for both potassium and sodium are plotted against values of $x$ varying from zero to 1 for each ion,[4] and for comparison the solid lines give the transference numbers according to the assumptions given above. Considering the difficult nature of the experimental work the agreement is remarkably good, especially for the transference numbers of the sodium ion. For 0.2 and 0.4 $N$ the agreement with the theory and of check determinations with one another is not so good. *The deviations of the observed values from the theoretical curve are, however, in no case greater than the variations of these values among themselves.* This is also true of the results at 0.8 and 1.6 $N$ which are not reproduced in the figures.

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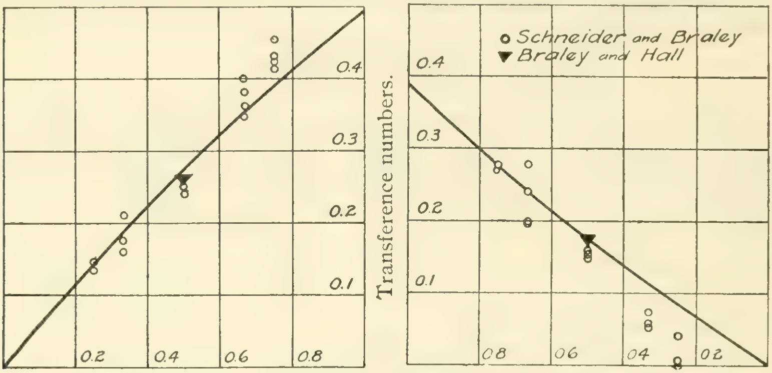
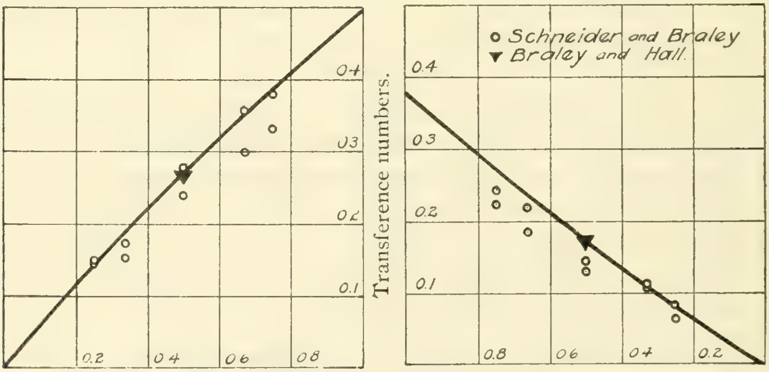
[3] It seems worth mentioning that the assumption that the transference numbers vary in the manner given in Equation 1, when combined with thermodynamic expressions, gives Lewis and Sargent's formula $E_{L} = RT/F \ln \Lambda/\Lambda'$, which represents accurately a large proportion of the values for the liquid junctions of two equally concentrated salt solutions with a common ion. In a boundary such as is given in a flowing junction, there are mixtures that vary in composition from $x = 0$ to $x = 1$. See MacInnes and Yeh, THIS JOURNAL, **43**, 2563 (1921).

[4] For the transference numbers of the cation of potassium and sodium chlorides at 0.1 *N* the values 0.492 and 0.387, respectively, were used. These numbers have been recently obtained in this Laboratory [Smith and MacInnes, THIS JOURNAL, **47**, 1009 (1925)]. For these constants at 0.2 *N* see the following article. For 0.4 *N*, I have interpolated, on a logarithmic scale, with these values and those of Washburn [*ibid.*, **31**, 322 (1909)] and have obtained the values 0.484 and 0.373.



Ratio—moles of KCl: total concn. Ratio—moles of NaCl: total concn.

Fig. 2.—0.2 $M$.



Ratio—moles of KCl: total concn. Ratio—moles of NaCl: total concn.

Fig. 3.—0.4 $M$.

The only series in which a systematic deviation of the results observed may possibly be greater than the experimental error, indicated in the results themselves, is at a total concentration of 0.2 $N$ (Fig. 2) with a small proportion of sodium chloride. Here, the measured amount of transference of sodium ion, according to these authors' results, drops nearly to zero. This could be accounted for by the motion of the positively charged sodium ion being nearly balanced by the movement of a negatively charged complex such as $(NaCl)_xCl_y$. Since the transference of sodium chloride was determined by the difference between the weights of the dried chlorides and the directly determined amount of potassium chloride, any error which would give too much of the latter would result in too little sodium chloride. It will be noted that the values of the transference numbers for potassium are high in this region. In another set of experiments, at this same concentration, greater variations between the various determinations are found than constitute the whole difference between the first mentioned results and the curve representing the theory. It does not appear, therefore, that the experiments at 0.2 *N* are of sufficient accuracy to give evidence as to whether complexes are or are not present in the solutions. It is, indeed, difficult to see how it is possible for the measurements to show this abnormal behavior at 0.2 *N* when there is substantial agreement at adjoining concentrations, that is, at 0.1 and 0.4 *N*; particularly, as is shown below, there is no evidence of anything unusual reflected in the conductance measurements. However, since Schneider and Braley have made more experiments at 0.2 *N* than at the other concentrations, and since the subject is of great importance, furnishing as it does a crucial test of the possibility of holding to any theory postulating simple ions, it has been considered desirable to repeat the work of these authors. The results of the latter investigation are given in an article by Jane Dewey,[5] immediately following this.

Some results of similar measurements, of a higher order of accuracy, judging from the agreement of check determinations, have been published by Braley and Hall[6] and the results of these measurements are indicated in the plots by small triangles. These points fall on, or very near to, the curves which represent the assumption of simple ions. Braley and Hall also consider that their results prove the presence of complexes. Their proof, however, rests upon deviations of the measured transference numbers from their theory, which is based upon the tacit assumption that the mobilities of the ions do not vary with the concentration. This would require that the transference numbers remain constant from infinite dilution to the concentration in question, whereas all of these numbers show marked variation with the concentration.

If the transference number varied with the composition of the solution in the complicated manner that Schenider and Braley consider that their results show, it would certainly be expected that some effect of these variations would be seen in the conductance measurements. Fig. 4 shows, however, that Stearn's[7] results for the conductance of mixtures of potassium and sodium chlorides yield smooth curves which are very nearly straight lines, when the conductances of the mixtures are plotted against values[8] of the ratio $x$. In a paper already referred to, I have presented evidence that the conductance of the chloride ion ($N_{\text{Cl}}\Lambda_{\text{MCl}}$) is the same when that ion is in solution with any of the alkali metals or hydrogen. This is true up to molal concentration if corrections are made for differences in viscosity. This observation is inconsistent with the presence of complexes in solutions of single salts unless they are of such a nature that they do not vary for such dissimilar substances as hydrochloric acid and cesium chloride, which seems hardly possible. The closely linear variation of the conductances of the mixtures, which was assumed in deriving Equations 1 and 2, appears to be good evidence that simple ions only are present in the mixtures.

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[5] Dewey, THIS JOURNAL, **47**, 1927 (1925).

[6] Braley and Hall, *ibid.*, **42**, 1770 (1920). These authors include a few figures that do not check with those plotted but give the same ratio of the potassium-to-sodium transference numbers.

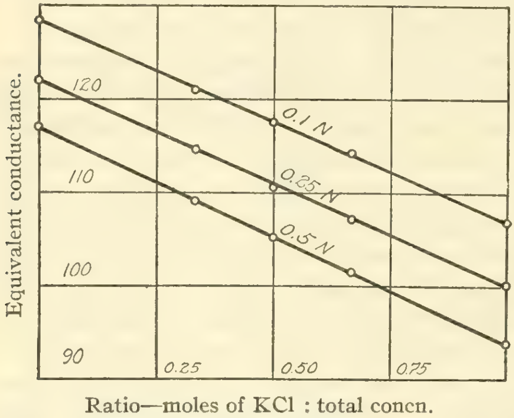

Fig. 4.—The conductances of potassium and sodium chloride solutions and their mixtures.

## Conclusion and Summary

Braley and Hall, and later Schneider and Braley, have published results of transference measurements on solutions of mixtures of sodium and potassium chlorides, which they hold to prove that ionic complexes such as $K_x(NaCl_2)_y$ are present in these solutions However, a reëxamination of these investigations leads to the conclusion that their data are in accord with the assumption that simple ions only are present in the solutions, within the experimental error, which for many of the results is quite large. The results of Schneider and Braley on mixtures at a total concentration of 0.2 $N$ indicate, however, sufficient divergence from the theory to make a redetermination desirable, the results of which are given in the following article.[5]

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[7] Stearn, THIS JOURNAL, **44,** 670 (1922).

[8] Schneider and Braley's own conductance measurements lead to similar straight lines when plotted as shown. The curves they give for a plot similar to Fig. 4 are due to the use of a scarcely defensible scale of abscissas. Also they give no comparative values for the conductances of the pure salts. Compared with published values for these constants their data appear to be high. Measurements on these mixtures at 0° by Dewey (following paper) indicate a maximum deviation of 0.3% from linearity at 0.2 $N$ and of 0.4% at 0.25 $N$.

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# THE MELTING POINT OF ICE ON THE ABSOLUTE TEMPERATURE SCALE

by

Leighton B. Smith and Robert S. Taylor

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# THE MELTING POINT OF ICE ON THE ABSOLUTE TEMPERATURE SCALE

By Leighton B. Smith and Robert S. Taylor

Received June 25, 1923

Chappuis,[1] Day and Clement,[2] Holborn and Henning[3] and Eumorfopoulos[4] have made measurements on the expansion coefficients from 0° to 100° both for the constant volume and the constant pressure thermometers. Keyes[5] calculated $\epsilon$, the expansion coefficient for a perfect gas, using the data of the above-mentioned workers and the equation of state which he based on Amagat's data for atmospheric nitrogen. Since then Henning,[6] and Henning and Heuse[7] have done some work on expansion coefficients for nitrogen and some other gases. It is, therefore, thought worth while to review the above data using the new equation of state of nitrogen[8] and also the method of obtaining $\epsilon$ using the equation of state, since this has never been given in detail before.

Instead of using a constant-pressure thermometer, a constant-$\pi$ thermometer will be considered where $\pi$ is defined by the equation $\pi\omega = RT$. From the Keyes equation of state $\omega = v - \delta$ or, for low pressures $\omega = v - \beta$ and $\pi = p + A/(v + l)^2$, which reduces at low pressures to the form, $\pi = p + (A/v^2)$.

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[1] Chappuis, *Trav. mem. bur. intern.*, **6,** 59 (1888) and **13,** 66 (1903).

[2] Day and Clement, *Am. J. Sci.*, **26,** 405 (1908).

[3] Holborn and Henning, *Ann. Physik*, **35,** 761 (1911).

[4] Eumorfopoulos, *Proc. Roy. Soc. London*, **90A,** 189–203 (1914).

[5] Keyes, This Journal, **42,** 54 (1920).

[6] Henning, *Z. Physik*, **5,** 264 (1921).

[7] Henning and Heuse, *ibid.*, **5,** 285 (1921).

[8] Smith and Taylor, This Journal, **45,** 2115 (1923).

Then $\epsilon$, the coefficient of expansion for a perfect gas, is given by the equation,

$$\epsilon = \left(\frac{\omega_t - \omega_0}{\omega_0\, t_{(ab)}}\right)_\pi \tag{1}$$

where $t_{(ab)} = T - T_0$ or, in other words, is centigrade thermodynamic temperature. The above equation is, therefore, identical with the following,

$$\epsilon = \frac{v_t{}^\pi - v_0}{(v_0 - \beta)\, t_{(ab)}} \tag{2}$$

where $v_0$ is the volume measured at 0° and $v_t^\pi$ is the volume at $t°$ when $\pi$ has the same value as at 0°.

$\epsilon_{p_0}^t$ is defined by the following equation,

$$\epsilon_{p_0}{}^t = \frac{v_t{}^p - v_0}{v_0 t_c} \tag{3}$$

where $v_t^p$ is measured on the constant-pressure thermometer. The constant-$\pi$ thermometer has never been investigated experimentally hence $v_t^\pi$ must be eliminated from Equation 2. By adding and subtracting $v_t^p$ from the numerator of Equation 2 the following is obtained.

$$\epsilon = \frac{(v_t{}^{p_0} - v_0) + (v_t{}^\pi - v_t{}^p)}{(v_0 - \beta)\, t_{(ab)}} \tag{4}$$

Dividing numerator and denominator by $v_0 t_c$, Equation 4 becomes

$$\epsilon = \left[\frac{\dfrac{v_t{}^{p_0} - v_0}{v_0 t_c} + \dfrac{v_t{}^\pi - v_t{}^{p_0}}{v_0 t_c}}{\left(1 - \dfrac{\beta}{v_0}\right)\dfrac{t_{ab}}{t_c}}\right]_\pi \tag{5}$$

Substituting from Equation 5

$$\epsilon = \left[\frac{\epsilon_p + \dfrac{v_t{}^\pi - v_t{}^{p_0}}{v_0 t_c}}{\left(1 - \dfrac{\beta}{v_0}\right)\dfrac{t_{ab}}{t_c}}\right]_\pi \tag{6}$$

Since $p_t^\pi$ is very close to $p_0$, Boyle's law may be assumed to hold without, in this instance, introducing too great an error, or $v_t^\pi p_t^\pi = v_t^{p_0} p_0$.

Hence $v_t^\pi = v_t^{p_0} \dfrac{p_0}{p_t^\pi}$. Using this relation, Equation 6 becomes

$$\epsilon = \frac{\epsilon_p + \dfrac{v_t{}^{p_0}}{v_0 t_c}\left[\dfrac{p_0}{p_t{}^\pi} - 1\right]}{\left[1 - \dfrac{\beta}{v_0}\right]\dfrac{t_{ab}}{t_c}} \tag{7}$$

Since $\dfrac{v_t^{p_0}}{v_0} = \left(1 + \epsilon_{p_{0°}}^{t°}\right)$ and since the pressures are involved only in the correction term, Equation 7 may be written

$$\epsilon = \frac{\epsilon_p + \dfrac{1 + \epsilon_p{}^t}{t_c}\left[\dfrac{p_0 - p_t{}^\pi}{p_t{}^\pi}\right]}{\left[1 - \dfrac{\beta\, t_{ab}}{v_0\, t_c}\right]} \tag{8}$$

Furthermore, $\pi_t = \pi_0$; therefore $p_t + \frac{A}{(v_t)^2} = p_0 + \frac{A}{(v_0)^2}$ or $p_t - p_0 = \frac{A}{v_0^2} - \frac{A}{v_t^2}$. But $v_t = v_0(1 + \epsilon_p t_c)$; therefore $p_t - p_0 = \frac{A}{v_0{}^2}\left[1 - \frac{1}{(1 + \epsilon_p t_c)^2}\right]$.

Therefore,[9] $$\frac{p_0 - p_t}{p_0} = -\frac{A}{p_0 v_0{}^2}\left[\frac{(1 + \epsilon_p t_c)^2 - 1}{(1 + \epsilon_p t_c)^2}\right] \qquad = -\frac{A\epsilon_p t_c}{p_0 v_0{}^2}\left[\frac{2 + \epsilon_p t_c}{(1 + \epsilon_p t_c)^2}\right].$$

Equation 8 now becomes,

$$\epsilon\left(1 - \frac{\beta}{v_0}\right)\frac{t_{ab}}{t_c} = \epsilon_p - \frac{A\epsilon_p}{p_0 v_0{}^2}\left[\frac{2 + \epsilon_p t_c}{1 + \epsilon_p t_c}\right] \tag{9}$$

Since $t_c = 100 - t_{ab}$ and since $p_0 v_0 = RT_0$, Equation 9 becomes

$$\epsilon = \epsilon_p + \frac{\beta\epsilon}{v_0} - \frac{A\epsilon_p}{R^2 T_0{}^2}\left[\frac{2 + \epsilon_p t_c}{1 + \epsilon_p t_c}\right] p_0 \tag{10}$$

or since in the correction term it suffices to say that $\epsilon_p = \epsilon = 1/T_0$,

$$\epsilon_p = \epsilon + \left[\frac{A}{R^2 T_0{}^3}\left(\frac{2 + \epsilon_p t_c}{1 + \epsilon_p t_c}\right) - \frac{\beta}{RT_0{}^2}\right] p_0 \tag{11}$$

It is now seen that with the aid of certain approximations which, however, are permissible since they involve only the correction factor, the limitation of the constant-$\pi$ thermometer has been removed and the resulting formula is general.

In the case of the constant-volume coefficient the same procedure is employed but the derivation is very much simplified, as will be seen. For the constant-$\omega$ thermometer

$$\epsilon = \left[\frac{\pi_t - \pi_0}{\pi_0\, t_{ab}}\right]_\omega = \left[\frac{p_t - p_0}{\left(p_0 + \frac{A}{v_0{}^2}\right)t}\right]_\omega,$$

since constant $\omega$ is identical with constant volume and $A/v^2$ is independent of the temperature. By definition,

$$\epsilon_v = \frac{p_t - p_0}{p_0 t}. \qquad \text{Hence,} \qquad \epsilon_v = \epsilon + \frac{A\epsilon}{v_0{}^2 p_0}, \qquad \text{or} \qquad \epsilon_v = \epsilon + \frac{A}{R^2 T_0{}^3} p_0. \tag{12}$$

From the equation of state of nitrogen, Equation 12 becomes $\epsilon_v = \epsilon + 0.00000029\ p_0$ (atm.). Since $1/\epsilon = T_0$, the absolute temperature of melting ice can be calculated from measured expansion coefficients.

In Table I are given the measured values of $\epsilon_p$, and calculated values of $T_0$. In Table II are the measured values of $\epsilon_v$ and calculated values of $T_0$.

It is seen from these tables that in no way can the above data be averaged to give a value of 273.20 as the ice point on the absolute centigrade scale as obtained by Henning and Heuse. The data of Henning and Heuse on nitrogen vary from an ice point of 273.130 to one of 273.231.

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[9] In Keyes' paper, THIS JOURNAL, **43**, 1461 (1921), there is a typographical error in this equation, the square term in the denominator of the expression in brackets being omitted.

An average of their data alone, however, gives 273.175°. A consideration of the other data leads one to believe that even this is too high by several hundredths of a degree. Keyes,[5] after a review of the data on coefficients

TABLE I

ABSOLUTE ICE-POINT TEMPERATURES COMPUTED FROM MEASURED CONSTANT PRESSURE EXPANSION COEFFICIENTS

| $p$ (atm.) | Therm. material | $e_p \times 10^3$ (obs). | $e$(calc.) | $T_0$(calc.) |
|---|---|---|---|---|
| 1.318 | Pt Ir | 3.67315[a] | 3.66121 | 273.134 |
| 1.825 | Pt Ir | 3.67775[a] | 3.66123 | 273.132 |
| 0.520 | Quartz | 3.66561[b] | 3.66090 | 273.157 |
| 0.546 | Quartz | 3.66587[b] | 3.66093 | 273.155 |
| 1.042 | Quartz | 3.67005[b] | 3.66061 | 273.179 |
| 1.032 | Quartz | 3.67019[b] | 3.66085 | 273.161 |
| 0.996 | Quartz | 3.66991[b] | 3.66089 | 273.158 |
| 0.289 | $59^{III}$ glass | 3.6630[c] | 3.66038 | 273.196 |
| 0.671 | $59^{III}$ glass | 3.6679[c] | 3.66082 | 273.163 |
| 1.460 | $59^{III}$ glass | 3.6742[c] | 3.66098 | 273.151 |

Mean of above values gives for $T_0$, 273.159.

[a] Ref. 1. [b] Ref. 4. [c] Ref. 7.

TABLE II

ABSOLUTE ICE-POINT TEMPERATURES COMPUTED FROM MEASURED CONSTANT VOLUME EXPANSION COEFFICIENTS

| $p$ (atm.) | Therm. material | $e_v \times 10^3$ | Observer | $e$(calc.) | $T_0$(calc.) |
|---|---|---|---|---|---|
| 1.044 | verre dur | 3.6718 | Chappuis (1902) | 3.66210 | 273.067 |
| 0.698 | verre dur | 3.6685 | Chappuis (1902) | 3.66202 | 273.073 |
| 1.310 | Pt Ir | 3.6747 | Chappuis (1887) | 3.66253 | 273.035 |
| 1.318 | Pt Ir | 3.6744 | Chappuis (1907) | 3.66215 | 273.064 |
| 0.742 | Quartz | 3.6699 | Chappuis (1914) | 3.66301 | 273.000 |
| 0.727 | Quartz | 3.66943 | Chappuis (1914) | 3.66267 | 273.025 |
| 0.740 | Quartz | 3.66959 | Chappuis (1914) | 3.66272 | 273.021 |
| 0.413 | Pt | 3.665 | Day and Clement | 3.66116 | 273.137 |
| 0.724 | Pt | 3.668 | Day and Clement | 3.66128 | 273.129 |
| 0.979 | Pt | 3.670 | Day and Clement | 3.66091 | 273.156 |
| 1.2961 | Pt | 3.673 | Day and Clement | 3.66095 | 273.153 |
| 0.8305 | $59^{III}$ glass | 3.6706 | Holborn and Henning | 3.66288 | 273.009 |
| 0.8175 | $59^{III}$ glass | 3.6699 | Holborn and Henning | 3.66231 | 273.052 |
| 0.8166 | Quartz | 3.66843 | Holborn and Henning | 3.66085 | 273.161 |
| 0.2895 | $59^{III}$ glass | 3.6626 | Henning and Heuse | 3.65991 | 273.231 |
| 0.6710 | $59^{III}$ glass | 3.6675 | Henning and Heuse | 3.66126 | 273.130 |
| 1.4605 | $59^{III}$ glass | 3.6752 | Henning and Heuse | 3.66062 | 273.178 |
| 0.800 | Quartz | 3.6687 | Keyes, Townshend, Young | 3.66127 | 273.129 |

Mean of the above gives $T_0$ = 273.097; omitting Chappuis' values, $T_0$ = 273.134, average of all nitrogen data gives $T_0$ = 273.119

of expansion for all gases for which data are available, reached the conclusion that $T_0$ = 273.14. Buckingham decided on 273.13. From the above data it is evident that 273.12° is about as good a value as can be obtained from the nitrogen coefficients alone. A paper will soon be forthcoming from this Laboratory dealing with the data on other gases, but for the present it appears that 273.13° is about as good a value for $T_0$ as can be decided upon.

In conclusion it is desired to thank Dr. Keyes for his valuable suggestions and assistance.

## Summary

The value of $T_0$, the absolute temperature of melting ice, from the nitrogen volume and pressure expansion coefficients gives a mean value of 273.12°. The mean value obtained by using the data of other gases including the Joule-Thomson coefficient is 273.13° ± .01°.

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Contribution from

Research Laboratory of Physical Chemistry

Serial No. 155 March, 1924

# THE PRESSURE-VOLUME-TEMPERATURE RELATION FOR GASEOUS ETHYL ETHER

by

James A. Beattie

not decompose sufficiently rapidly to cause any inconvenience. The inner vessel contained a tightly fitting steel top with split plugs for the introduction of the necessary parts.

The bath was thoroughly stirred by means of a set of propeller blades which drew the oil down through a steel tube, at the top of which was a heating coil, and forced it out at the bottom against the regulator. The latter was a thin steel tube filled with mercury, having at the top the usual means for operating a relay, which controlled the flow of current in the internal heating coil.

Enough current was constantly passed through the external coil to raise the temperature of the bath to within about 2° of the desired temperature, the rest of heating being accomplished in the internal coil, and was regulated as described above.

The temperature was measured by a platinum thermometer of the flat type, resistances being measured on a Mueller bridge. The bridge was thermostatted and the resistances calibrated just before the measurements. The ice point of the thermometer was measured each day and the steam benzophenone and naphthaline points determined from time to time, satisfactory checks being obtained throughout the period over which the measurements extended.

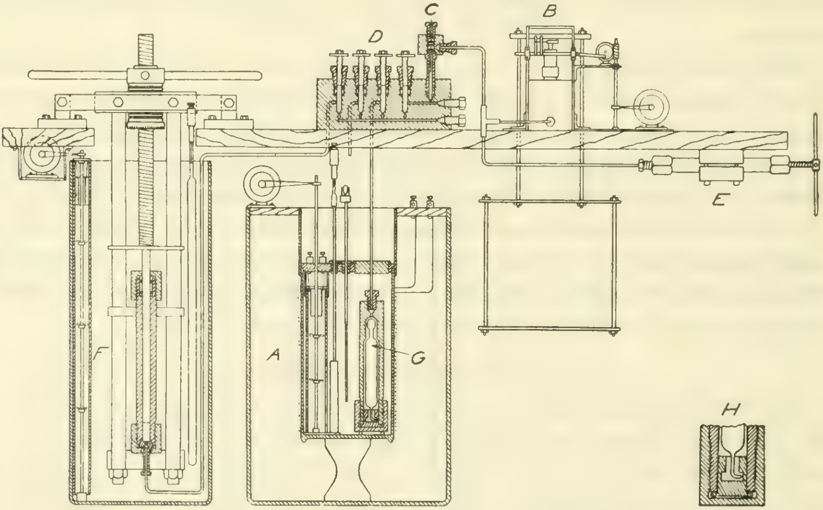

Fig. 1.—The compressibility apparatus.

The automatic regulation of the bath temperature was satisfactory to 300°, constancy to ±0.002° being obtained; but at 325° hand regulation was used, a switch operated by hand taking the place of the relay, in which case a temperature variation of ±0.005° was allowed.

The piezometer containing the gas was placed in the thermostat in such a manner that the bath fluid could circulate around it in all directions.

**The Pressure Gage.**—The gage, B, Fig. 1, was of the dead-weight piston type with mechanical oscillation, similar to that used by Keyes and Brownlee.[6] The piston constant was about 0.734 mm. of mercury at standard conditions per gram weight on the pan.

The gage was calibrated against a mercury column. The temperature of the column was kept as constant as possible by enclosing it in a channel-shaped wooden frame, the front of which was closed with heavy cardboard. The temperature was obtained by averaging the readings of a series of mercury thermometers placed one meter apart, and the length of the mercury column was measured on a steel scale kept under a constant tension, which was also applied when calibrating it against a standard meter. Two different grades of oil—"Lard" and "Heavy Medium" designated by L. and H. M. in the table—were used to lubricate the piston, but no specific effect due to the oil could be detected. Table I contains a résumé of the calibration data. In the third column is given the height of the mercury corrected for the tape error; in the fourth, this height has been reduced to 0°, 45° latitude and sea level. In Col. 5 is the correction for the oil levels and the weight of a column of air equivalent to that of the mercury height; in Col. 6 is the correction for the compressibility of the mercury, and in Col 7 is the fully corrected height of the column while in Col. 8 is the total weight on the piston.

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[6] Keyes and Brownlee, THIS JOURNAL, **40**, 25 (1918).

TABLE I

CALIBRATION OF THE PISTON GAGE

| Oil | Mean temp. of column °C. | True height in mm. | Height under standard cond. Mm. | Oil and air heights corr. Mm. | Compressibility corr. Mm. | Corr. height in mm. | Total wt. on pan G. | Piston constant Mm./g. | Deviation from mean $\times 10^5$ |
|---|---|---|---|---|---|---|---|---|---|
| H. M. | 21.19 | 8953.4 | 8916.81 | −56.77 | +0.20 | 8860.24 | 12070.01 | 0.734071 | +4.7 |
| H. M. | 22.83 | 8956.9 | 8917.64 | −56.77 | .20 | 8861.07 | 12072.01 | .734018 | −0.6 |
| H. M. | 21.61 | 8961.4 | 8924.11 | −56.77 | .20 | 8867.54 | 12081.21 | .733994 | −3.0 |
| H. M. | 20.12 | 8955.9 | 8921.03 | −56.77 | .20 | 8864.46 | 12076.31 | .734037 | +1.3 |
| L. | 21.71 | 9006.4 | 8968.75 | −57.22 | .20 | 8911.73 | 12141.01 | .734019 | −0.5 |
| L. | 21.64 | 6987.8 | 6958.68 | −57.04 | .12 | 6901.76 | 9402.74 | .734016 | −0.8 |
| L. | 21.73 | 5001.6 | 4980.68 | −56.86 | .06 | 4923.88 | 6707.98 | .734033 | +0.9 |
| L. | 22.86 | 8997.4 | 8957.93 | −57.22 | .20 | 8900.91 | 12126.71 | .733992 | −3.2 |
| H. M. | 20.92 | 9007.9 | 8971.53 | −56.78 | .20 | 8914.95 | 12145.01 | .734042 | +1.8 |
| H. M. | 21.27 | 6992.3 | 6963.63 | −56.60 | .12 | 6907.15 | 9409.72 | .734044 | +2.0 |
| H. M. | 22.40 | 9011.4 | 8972.61 | −56.78 | .20 | 8916.03 | 12147.01 | .734010 | −1.4 |
| L. | 20.20 | 9001.4 | 8966.23 | −56.78 | .20 | 8909.65 | 12138.11 | .734023 | −0.1 |
| L. | 20.74 | 9011.4 | 8975.31 | −56.78 | .20 | 8918.73 | 12150.01 | .734051 | +2.7 |
| H. M. | 20.69 | 6990.8 | 6962.86 | −56.60 | .12 | 6906.38 | 9409.22 | .734001 | −2.3 |
| H. M. | 21.88 | 6992.8 | 6963.36 | −56.60 | .12 | 6906.88 | 9409.72 | .734015 | −0.9 |
|  |  |  |  |  |  |  | Av. | .734024 | ±1.7 |

Piston constant, 0.73402 ± 0.00002 mm./g.

To determine when pressure equilibrium had been reached, the device shown at C, Fig. 1, was used.

This consisted of a steel needle projecting into a capillary, and insulated electrically from the rest of the block. Mercury filled the block D to the point of the needle, the position of which was not affected by pressure, and above was oil which communicated the pressure to the piston gage. The oil leak at the gage was compensated for by addition from the injector shown at E.

The steel needle and the block D were connected in series with a telephone and the 2-volt terminals of a transformer. When there was not sufficient weight on the pan to balance the pressure in the piezometer the mercury level rose at C and made contact with the needle, causing a buzzing in the telephone; when too much weight was on the pan the circuit was broken. This gave a delicate means of detecting pressure equilibrium, as at pressures below 50 atmospheres 1 g. was sufficient to cause the circuit to make or break.

**The Volume Measuring Device.**—The volume of the gas in the piezometer G, Fig. 1, was varied by the injection of mercury from the compressor F.

This consisted of a very uniform steel rod passing through a packing into a thick steel tube filled with mercury. The packing was linen cloth soaked in ceresin wax, at the top and bottom of which were hard rubber rings to prevent the piston from dragging any of the wax with it. The piston was moved in and out by means of a threaded portion passing through a long Tobin bronze nut, at the upper and lower surfaces of which were roller bearings to reduce the friction and wear of turning the nut. At the lower end the head of the nut was divided into a hundred parts, and also a revolution counter was attached, so that the number of whole turns and fractions could be determined. The piston was 22.2 mm. ($^7/_8$ in.) in diameter, and the pitch of the thread was 10 in 14 mm. (18 per inch) so that a thousandth of a turn, which could be easily estimated, varied the volume by about 0.5 cu. mm.

The temperature of the compressor was kept constant by a kerosene bath, which was stirred, heated and regulated as shown in Fig. 1, and it was measured with a platinum thermometer, the regulation being to ±0.001°, while the bath temperature was 30°.

The piston was calibrated by weighing the amount of mercury expelled for each ten turns, using an extremely fine glass tip cemented to the end of the steel capillary leading from the compressor.

In making a measurement, mercury was expelled from the compressor and passed through a capillary to the block D, containing 4 steel stopcocks, one shutting off the compressor, one the piezometer, one the piston gage, and one leading to a vacuum pump. In the block and connecting steel capillaries was about 1.5 cc. of mercury. The temperature of the block was measured, and correction for the thermal expansion made.

From the block the mercury passed down through a capillary and between the steel and glass vessels G, then up through the glass capillary and into the gas space.

**The Piezometer.**—It has been found that ether decomposes at high temperatures when in contact with iron, but no decomposition takes place at 325° when held in glass containers. Hence the piezometer G consisted of a glass vessel of about 96 cc. capacity surrounded by a steel jacket.

The piezometer was made of Pyrex glass and annealed. At one end was a small bulb connected to the main part of the vessel by a capillary. This bulb and capillary were calibrated with mercury, since it was intended to determine the amount of ether present by measuring the volume of the liquid phase at 0°, where the density is accurately known, and correcting for the amount of the gas phase in the main portion of the piezometer. At the other end was a fine capillary. The volume of the piezometer was determined for various heights, and also its total capacity at 30°, as well as the volume per unit length of the capillaries.

The steel bomb was closed by a soft steel-washer, made by heating cold rolled steel to 1100° in a stream of hydrogen.[7] It was confined between the body and cap of the bomb in such a way that it could not flow. The lock nut was separate from the cap, so that in tightening, the latter would not turn on the washer and scar it. This joint has been opened and closed, heated to 325° many times, and subjected to a pressure of 1000 atmospheres without leaking.

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[7] This washer was suggested by Dr. Keyes and, as stated above, gave excellent results.

## Method of Filling the Piezometer

The ether was purified by shaking with concd. sulfuric acid, then treating it several times with an alkaline permanganate solution, and washing it with water after each treatment. This was followed by treatment with sulfuric acid, calcium chloride, and finally by several distillations from sodium.

Dry ether was introduced into Flasks AA, Fig. 2, and distilled back and forth many times. It was frozen after each distillation by means of liquid air, and evacuated each time with a diffusion pump. The purpose of this was to remove all traces of dissolved gases that might have been present. At B is shown a device similar to that used by Young[8] to test the completeness of the removal of air. It consisted of an inverted bell which could be raised by a magnet, thus collecting some of the gas phase. If this disappears promptly under the small hydrostatic pressure of the liquid phase, it is taken to indicate the absence of permanent gases.

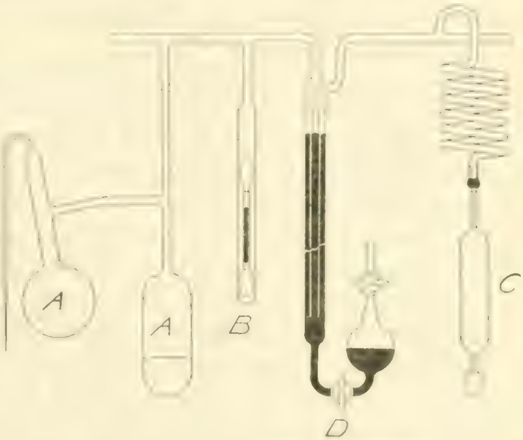

Fig. 2.—The loading apparatus.

The piezometer C was connected to the filling apparatus by a cement and evacuated for two days, while being heated constantly to 360°. It was then connected to the ether supply by means of the greaseless stopcock at D, the ether distilled in, and frozen by means of liquid air. The piezometer was sealed off as near the line to which it had been calibrated as possible and the capillary bent as shown at H, Fig. 1.

The amount of ether present was determined both by measuring the volume of liquid present and correcting for the amount of vapor as described above, and by direct weighing, using a vessel similar in shape to the piezometer as a counterpoise. These weighings extended over two weeks with widely different room temperatures and barometric pressures. The results were concordant to 0.1 mg., and the two methods agreed to 0.2 mg.

## Experimental Method

A blank run was first made to determine the compressibility of the apparatus. The glass piezometer was evacuated, sealed off, and placed in the steel casing, the bend in the capillary fitting into a slot in the cap of the bomb as shown at H, Fig. 1.

The bomb was closed, connected to the block D, and placed on its side in a thermostat at 30°. The compressor was so filled that mercury just appeared on the end of its capillary when the reading on the head was zero. The piston was withdrawn slightly and the capillary also attached to the block D.

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[8] Young, *Phil. Mag.*, 20, 797 (1910).

The block and the space around the glass piezometer were then evacuated, the pressure gage B being disconnected and a blank plug substituted. The vacuum was shut off and mercury forced into the bomb from the compressor, until the space around the piezometer and also the block up to the detection needle at C were filled. The gage was connected, and with each of the three stopcocks open exactly one turn several measurements at different pressures were made. From these data, by extrapolation, could be obtained the compressor setting, for the case that the pressure outside the piezometer was the same as that inside, namely a vacuum. This was called the "zero set."

The bomb was then set upright, and the glass piezometer in rising up broke the capillary at a point where a file scratch had been previously made. Mercury was run in until the vessel was completely filled. The compressibility of the whole apparatus was determined at 30° and at each of the temperatures used in the final measurements. From a plot of compressibility in terms of $\Delta v$ (volume of mercury in bomb at any temperature and pressure minus that present at 30° and zero pressure—the "zero set") against the pressure, for each isotherm, the change in volume due to the temperature and pressure in question could be read off.

The bomb was opened and filled with ether, and care was taken to have as nearly as possible the same amount of glass present as in the blank run. A zero set was again made at 30° but this time the extrapolation was made to the vapor pressure of the ether, in order to have the pressure inside and outside the piezometer the same. The measurements were then made on the compressibility of the ether vapor, the piston settings being made so that at each temperature the gas occupied precisely the same set of volumes, thus giving isometrics as well as isotherms.

The observed pressure was corrected for the barometric height, the oil level difference between the gage and the needle point, and the mercury level difference between the needle point and the height of the mercury in the piezometer, as well as the capillary depression of the mercury in the capillary at the detecting needle. The level of the mercury inside the piezometer was determined from a plot of the height against volume of mercury in the lower part of the piezometer made from the original calibration of the vessel. For any piston setting the amount of mercury in the piezometer was known, hence its height in the vessel was determined from the plot. For purposes of reducing the height of the mercury column to zero its temperature was divided into three sections. The application of these corrections which are accurately determinable give the pressure exerted by the gas at the temperature and volume in question.

The same amount of mercury was in the system during the final measurements as in the calibrations, since the compressor was also filled to the end of the capillary for each set of measurements and the block D completely cleaned out after each set. The volume of the glass in the piezometer was slightly different in the two sets of runs. A correction for this, which, however, was too small to affect the results, was applied.

To calculate the compressor setting for a desired density of gas, it was necessary to know approximately the pressure exerted by the substance for the specific volume and temperature in question. For this purpose the equation of state based on the work of Ramsay and Young was used. From the plot of the compressibility of the apparatus against pressure at each temperature could then be obtained the change in volume $\Delta v$ from the zero set at 30° due to the temperature and pressure expansion of the steel and the mercury. Suppose it is desired to cause the gas to occupy a space $V$. A correction must be applied due to the fact that in the preliminary runs this space was occupied by mercury at the temperature $T$ of the piezometer, whereas in the final measurements this mercury was in the compressor at 30°, where it occupied a smaller volume. Hence the volume $V$ must be multiplied by the ratio of the density of mercury at $t$° to that at 30°. A further slight correction is necessary since the compressibility of mercury is a function of temperature as well as pressure. The densities used were obtained from Landolt and Börnstein's "*Tabellen*," and the temperature function of compressibility from the work of Bridgman.[9] The latter correction was too small to affect the results appreciably. There is then added the compressibility of the apparatus, $\Delta v$, obtained as described above.

Subtracting this corrected volume from the inside volume of the piezometer at 30° gave the amount of mercury that must be injected from the zero set to give the desired space for the gas. The setting of the compressor could then be determined from its calibration.

## The Experimental Data

As stated in the introduction, the data were taken along isometrics in order to test, among other things, the linearity of the constant-volume lines. For each density an equation of the form

$$p = \psi T - \phi \tag{1}$$

was determined. In Table II are given the observed data together with the pressures calculated from the best straight line that can be put through the isometrics. The constants of this line are also given. The value of 0° on the absolute temperature scale was taken as 273.13°. It can be seen that for the smaller densities the observed data lie on a straight line within the experimental error, which it is believed is about 0.01 atmosphere up to 50 atm. However, at 12 cc. per g. a curvature of the measured isometric is clearly shown and this increases as the density becomes greater.

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[9] Bridgman, *Proc. Am. Acad.*, **57**, 347 (1911).

Table II

Comparison of Observed Pressures with Those Calculated by Assuming the Isometric Lines to be Straight

Temperatures in °C. The first line gives the observed pressure; the second is that calculated and the third is the first minus the second.

| Volume cc./g. | 150 | 175 | 200 | 225 | 250 | 275 | 300 | 325 |
|---|---|---|---|---|---|---|---|---|
| $p=0.03698T-4.460$ | | | | | | | | |
| 35 | 11.190 | 12.112 | 13.049 | 13.957 | 14.890 | 15.796 | 16.732 | 17.665 |
| | 11.187 | 12.112 | 13.036 | 13.961 | 14.885 | 15.810 | 16.734 | 17.659 |
| | 0.003 | 0.000 | 0.013 | −0.004 | 0.005 | −0.014 | −0.002 | 0.006 |
| $p=0.04416T-6.033$ | | | | | | | | |
| 30 | 12.667 | 13.756 | 14.847 | 15.966 | 17.076 | 18.165 | 19.276 | 20.394 |
| | 12.652 | 13.756 | 14.860 | 15.964 | 17.068 | 18.172 | 19.276 | 20.380 |
| | 0.015 | 0.000 | −0.013 | 0.002 | 0.008 | −0.007 | 0.000 | 0.014 |
| $p=0.05468T-8.644$ | | | | | | | | |
| 25 | 14.479 | 15.859 | 17.229 | 18.604 | 19.958 | 21.322 | 22.708 | 24.050 |
| | 14.493 | 15.860 | 17.227 | 18.594 | 19.961 | 21.328 | 22.695 | 24.062 |
| | −0.014 | −0.001 | 0.002 | 0.010 | −0.003 | −0.006 | 0.013 | −0.012 |
| $p=0.07140T-13.315$ | | | | | | | | |
| 20 | 16.880 | 18.678 | 20.471 | 22.250 | 24.038 | 25.841 | 27.601 | 29.390 |
| | 16.896 | 18.681 | 20.466 | 22.251 | 24.036 | 25.821 | 27.606 | 29.391 |
| | −0.016 | −0.003 | 0.005 | −0.001 | 0.002 | 0.020 | −0.005 | −0.001 |
| $p=0.10145T-22.962$ | | | | | | | | |
| 15 | .... | 22.492 | 25.036 | 27.578 | 30.120 | 32.639 | 35.194 | 37.713 |
| | .... | 22.501 | 25.037 | 27.573 | 30.110 | 32.646 | 35.182 | 37.718 |
| | .... | −0.009 | −0.001 | 0.005 | 0.010 | −0.007 | 0.012 | −0.005 |
| $p=0.12730T-32.203$ | | | | | | | | |
| 12.5 | .... | 24.825 | 28.023 | 31.214 | 34.400 | 37.586 | 40.755 | 43.930 |
| | .... | 24.844 | 28.026 | 31.209 | 34.391 | 37.574 | 40.756 | 43.939 |
| | .... | −0.019 | −0.003 | 0.005 | 0.009 | 0.012 | −0.001 | −0.009 |
| $p=0.16851T-48.138$ | | | | | | | | |
| 10 | .... | .... | 31.579 | 35.808 | 40.028 | 44.238 | 48.430 | 52.638 |
| | .... | .... | 31.589 | 35.802 | 40.015 | 44.227 | 48.440 | 52.653 |
| | .... | .... | −0.010 | 0.006 | 0.013 | 0.011 | −0.010 | −0.015 |
| $p=0.24374T-79.797$ | | | | | | | | |
| 7.5 | .... | .... | 35.502 | 41.626 | 47.730 | 53.805 | 59.908 | 65.973 |
| | .... | .... | 35.524 | 41.617 | 47.711 | 53.804 | 59.898 | 65.991 |
| | .... | .... | −0.022 | 0.009 | 0.019 | 0.001 | 0.010 | −0.018 |
| $p=0.41145T-155.869$ | | | | | | | | |
| 5 | .... | .... | 38.775 | 49.107 | 59.378 | 69.718 | 79.936 | 90.182 |
| | .... | .... | 38.800 | 49.087 | 59.373 | 69.659 | 79.945 | 90.232 |
| | .... | .... | −0.025 | 0.020 | 0.005 | 0.059 | −0.009 | −0.050 |
| $p=1.26107T-548.036$ | | | | | | | | |
| 2.5 | .... | .... | 48.490 | 80.221 | 111.821 | 143.296 | 174.608 | 206.100 |
| | .... | .... | 48.614 | 80.141 | 111.668 | 143.194 | 174.721 | 206.248 |
| | .... | .... | −0.124 | 0.080 | 0.153 | 0.102 | −0.113 | −0.148 |

Pressures in atmospheres $T=t$ °C. + 273.13

The accuracy of the equation of state can now be examined in the light of the data given in Table II. This equation has the form

$$p = \frac{RT}{v-\delta} - \frac{A}{v^2}e^{-(m/v)} \quad \text{where } \delta = \beta e^{-(\alpha/v)} \tag{2}$$

which requires the pressure to vary linearly with the temperature at constant volume. It should be borne in mind that in this form the equation[2,5] holds only when the molecular species of the fluid under consideration does not vary. When the association or dissociation is occurring (and it is assumed that when the isometrics begin to show curvature, this is what is taking place) the Keyes equation in this *particular* form is not applicable.

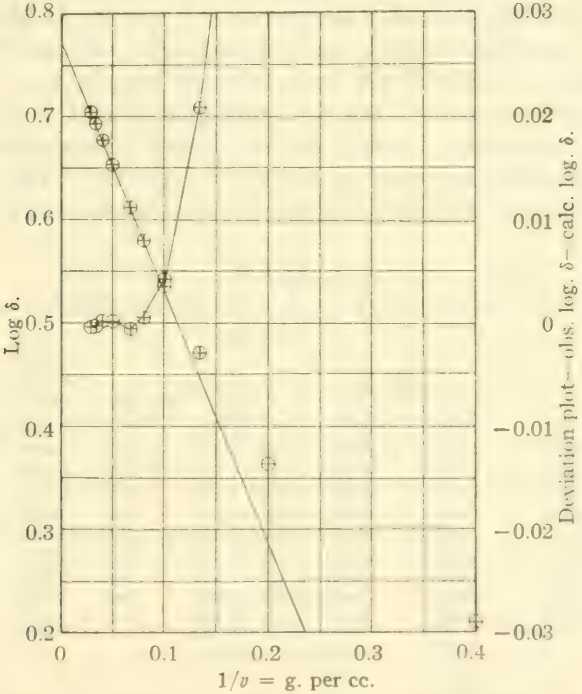

Fig. 3.—Plot of $\log_{10}\delta$ against $1/v$ and deviation plot. The equation of the straight line is $\log_{10}\delta = 0.77325 - \frac{2.4240}{v}$.

The $\psi$ and $\phi$ of Equation 1 become $\frac{R}{v-\delta}$ and $\frac{A}{v^2}e^{-m/v}$ and the accuracy of these functions can be tested for those densities for which the measured isometrics are substantially straight.

$$\text{Since } \psi = \frac{R}{v-\delta} \tag{3}$$

the value of $\delta$ can be calculated for the set of values of $\psi$ and $v$ given in Table II. In this case $R$ is the gas constant in cc. per atm. per degree C., and per gram and is for ether 1.1074, since its value in cc. per atm. per degree C. and per mole was taken as 82.056, and the molecular weight of ether as 74.096 (H = 1.0076, O = 16, C = 12.005). In Table III are given the values of $\delta$ so calculated (under the column headed "$\delta$ obs.") together with the corresponding specific volumes. To test the accuracy of the function used to represent $\delta$, a graph of log $\delta$ against $1/v$ was made. This, according to the equation of state, should be a straight line. Hence, a straight line was passed through the points and a deviation plot of $\Delta$ log $\delta$ against $1/v$ made (Fig. 3). The equation of the straight line chosen is given in Table III, together with the values of $\delta$ and log $\delta$ calculated from it. It will be seen that the delta function holds very satisfactorily in the region in which the isometrics are straight lines, that is, from larger specific volumes to 15 cc. per g., (and it is quite good even at 10 cc. per g.) but as the isometrics begin to curve, the discrepancy between the observed and calculated deltas increases, as would be expected. The values for the greater densities are, however, given to complete the table.

TABLE III

COMPARISON OF OBSERVED $\delta$ AND $\left(\frac{\partial P}{\partial T}\right)_v$ WITH THAT CALCULATED FROM THE EQUATION OF STATE

| Volume | Log $\delta$ | | | $\delta$ in cc. | | | $\left(\frac{\partial P}{\partial T}\right)_v$ in atm. per °C. | | |
|---|---|---|---|---|---|---|---|---|---|
| Cc./g. | Obs. | Calc. | Obs.-calc. | Obs. | Calc. | Obs.-calc. | Obs. | Calc. | Obs.-calc. |
| 35 | 0.70364 | 0.70399 | −0.00035 | 5.054 | 5.058 | −0.004 | 0.03698 | 0.03698 | 0.00000 |
| 30 | .69223 | .69245 | − .00022 | 4.923 | 4.926 | − .003 | .04416 | .04417 | − .00001 |
| 25 | .67651 | .67629 | .00022 | 4.748 | 4.746 | .002 | .05468 | .05468 | .00000 |
| 20 | .65225 | .65205 | .00020 | 4.490 | 4.488 | .002 | .07140 | .07139 | .00001 |
| 15 | .61109 | .61165 | − .00056 | 4.084 | 4.089 | − .005 | .10145 | .10149 | − .00004 |
| 12.5 | .57990 | .57933 | .00057 | 3.801 | 3.796 | .005 | .12730 | .12723 | .00007 |
| 10 | .53504 | .53085 | .00419 | 3.428 | 3.395 | .033 | .16851 | .16766 | .00085 |
| 7.5 | .47085 | .45005 | .02080 | 2.957 | 2.819 | .138 | .24375 | .23657 | .00717 |
| 5 | .36342 | .28845 | .07497 | 2.309 | 1.943 | .366 | .41145 | .36225 | .04920 |
| 2.5 | .21005 | − .19635 | .40640 | 1.622 | 0.636 | .986 | 1.26107 | .59410 | .66697 |

$\log \delta = 0.77325 - \frac{2.4240}{v}$; $\delta = 5.9327e^{-5.5815/v}$.

$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v - \delta} = \frac{1.1074}{v - \delta}$.

In Tables IV and V are given the data used in examining the two forms for the $\phi$ values. For the algebraic form $\phi = \frac{A}{(v+1)^2}$, it is necessary only to write $v + 1 = \sqrt{A}/\sqrt{\phi}$ and it can then be seen that a plot of $1/\sqrt{\phi}$ against $v$ should be a straight line. This graph is given in Fig. 4, and in Table IV are the values of $1/\sqrt{\phi}$ and $\phi$ obtained from Table II together with those calculated from the equations, $1/\sqrt{\phi} = 0.009714 + 0.013235\ v$ and $\phi = 5709/(v + 0.734)^2$. For the exponential form $\phi = \frac{A}{v^2} e^{-m/v}$ can be written $\log v^2\phi = \log A - \frac{2.3m}{v}$, and hence the log $v^2\phi$ should vary linearly with $1/v$. The plot is given in Fig. 5 and the observed and calculated values of log $v^2\phi$ and $\phi$, in Table V. The equations used are log $v^2\phi = 3.75656 - \frac{0.6375}{v}$, and $\phi = \frac{5709}{v^2}e^{-1.468/v}$. It can be seen that in

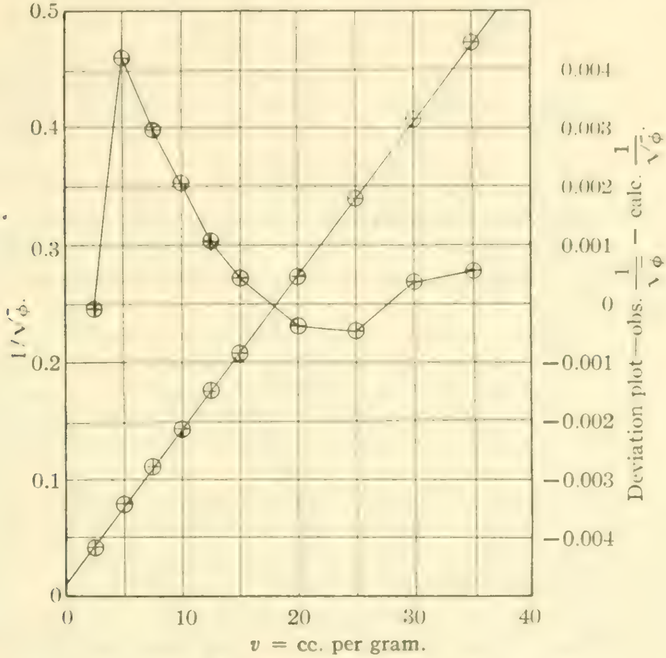

Fig. 4.—Plot of $\frac{1}{\sqrt{\phi}}$ against $v$ and deviation plot. The equation of the straight line is $\frac{1}{\sqrt{\phi}}$ = 0.009714 − 0.013235 $v$.

TABLE IV

COMPARISON OF OBSERVED $\phi$ WITH THAT CALCULATED FROM ALGEBRAIC FORM OF THE EQUATION OF STATE

| Volume | $\frac{1}{\sqrt{\phi}}$ | | | $\phi$ in atms. | | |
|---|---|---|---|---|---|---|
| Cc., g. | Obs. | Calc. | Obs.-calc. | Obs. | Calc. | Obs.-calc. |
| 35 | 0.47351 | 0.47294 | 0.00057 | 4.460 | 4.471 | − 0.011 |
| 30 | .40713 | .40676 | .00037 | 6.033 | 6.044 | − .011 |
| 25 | .34013 | .34059 | − .00046 | 8.644 | 8.621 | .023 |
| 20 | .27405 | .27441 | − .00036 | 13.315 | 13.280 | .035 |
| 15 | .20869 | .20824 | .00045 | 22.962 | 23.061 | − .099 |
| 12.5 | .17622 | .17515 | .00107 | 32.203 | 32.597 | − .394 |
| 10 | .14413 | .14206 | .00207 | 48.138 | 49.549 | − 1.411 |
| 7.5 | .11195 | .10898 | .00297 | 79.797 | 84.205 | − 4.408 |
| 5 | .080098 | .075889 | .004209 | 155.869 | 173.638 | −17.769 |
| 2.5 | .042716 | .042802 | − .000086 | 548.036 | 545.858 | 2.178 |

$\frac{1}{\sqrt{\phi}}$ = 0.009714 + 0.013235 $v$; $\phi = \frac{5709}{(v + 0.734)^2}$

the gas phase there is little choice between these two equations for $\phi$, the exponential type holding perhaps slightly better for the larger densities,

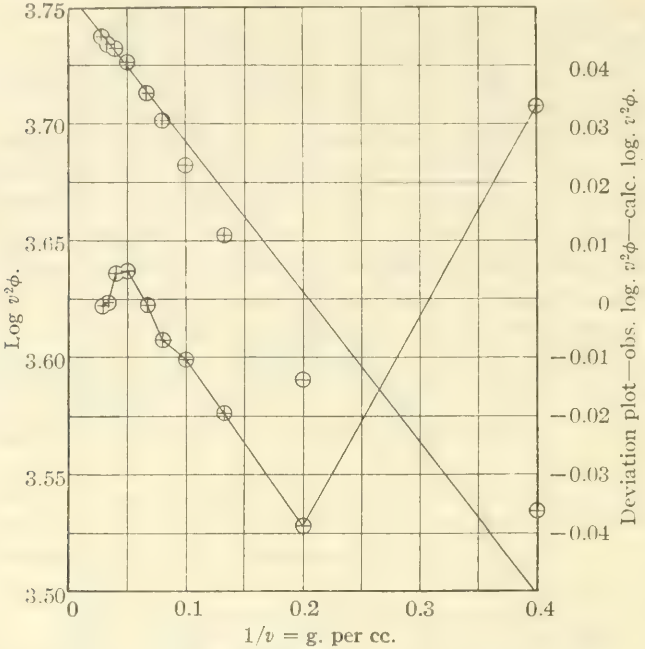

Fig. 5.—Plot of $\log_{10} v^2\phi$ against $1/v$ and deviation plot. The equation of the straight line is $\log_{10} v^2\phi = 3.75656 - \frac{0.6375}{v}$.

but both giving good results down to volumes of 15 cc. per g. Exactly the same value of A was used for the two equations, and $m$ was taken as exactly twice l.

TABLE V

COMPARISON OF OBSERVED $\phi$ WITH THAT CALCULATED FROM EXPONENTIAL FORM OF EQUATION OF STATE

| Volume Cc./g. | log $\phi v^2$ | | | $\phi$ in atmospheres | | |
|---|---|---|---|---|---|---|
| | Obs. | Calc. | Obs.-calc. | Obs. | Calc. | Obs.-calc. |
| 35 | 3.73747 | 3.73835 | −0.00088 | 4.460 | 4.469 | − 0.009 |
| 30 | 3.73478 | 3.73531 | − .00053 | 6.033 | 6.041 | − .008 |
| 25 | 3.73259 | 3.73106 | .00153 | 8.644 | 8.614 | .030 |
| 20 | 3.72640 | 3.72468 | .00172 | 13.315 | 13.262 | .053 |
| 15 | 3.71319 | 3.71406 | − .00087 | 22.962 | 23.008 | − .046 |
| 12.5 | 3.70172 | 3.70556 | − .00384 | 32.203 | 32.489 | − .286 |
| 10 | 3.68249 | 3.69281 | − .01032 | 48.138 | 49.296 | − 1.158 |
| 7.5 | 3.65211 | 3.67156 | − .01945 | 79.797 | 83.453 | − 3.656 |
| 5 | 3.59070 | 3.62906 | − .03836 | 155.869 | 170.263 | −14.394 |
| 2.5 | 3.53469 | 3.50156 | .03313 | 548.036 | 507.785 | 40.251 |

$$\log \phi v^2 = 3.75656 - \frac{0.6375}{v};\ \phi = \frac{5709}{v^2}\, e^{-1.468/v}$$

The Keyes equation for ether vapor becomes, therefore,

$$p = \frac{1.1074}{v-\delta}T - \frac{5709}{(v+0.734)^2}; \qquad \delta = 5.9327\,e^{-5.5815/v}$$

$$\text{or } \log\delta = 0.77325 - \frac{2.4240}{v} \qquad \text{(A)}$$

$$T = t°\text{C.} + 273.13$$

and the equation as modified by Phillips

$$p = \frac{1.1074}{v-\delta}T - \frac{5709}{v^2}e^{-1.468/v} \quad \text{where } \log v^2\phi = 3.75656 - \frac{0.6375}{v} \qquad \text{(B)}$$

$\phi$ being the second term on the right hand side of the equation.

In Table VI are given the values of the pressures calculated from Equation B, together with those measured in the present investigation. It can be seen that to a specific volume of 15 cc. per g., (that is, in the region

### TABLE VI

COMPARISON OF OBSERVED PRESSURE WITH THAT CALCULATED BY THE EQUATION OF STATE

Temperatures in °C. In the first line is the observed pressure in atmospheres; in the second that calculated; and the third is the first minus the second.

| Volume Cc./g. | 150 | 175 | 200 | 225 | 250 | 275 | 300 | 325 |
|---|---|---|---|---|---|---|---|---|
| 35 | 11.190 | 12.112 | 13.049 | 13.957 | 14.890 | 15.796 | 16.732 | 17.665 |
| | 11.178 | 12.103 | 13.027 | 13.952 | 14.876 | 15.801 | 16.725 | 17.650 |
| | 0.012 | 0.009 | 0.022 | 0.005 | 0.014 | −0.005 | 0.007 | 0.015 |
| 30 | 12.667 | 13.756 | 14.847 | 15.966 | 17.076 | 18.165 | 19.276 | 20.394 |
| | 12.649 | 13.753 | 14.857 | 15.961 | 17.066 | 18.170 | 19.274 | 20.378 |
| | 0.018 | 0.003 | −0.010 | 0.005 | 0.010 | −0.005 | 0.002 | 0.016 |
| 25 | 14.479 | 15.859 | 17.229 | 18.604 | 19.958 | 21.322 | 22.708 | 24.050 |
| | 14.523 | 15.890 | 17.257 | 18.624 | 19.991 | 21.358 | 22.725 | 24.092 |
| | −0.044 | −0.031 | −0.028 | −0.020 | −0.033 | −0.036 | −0.017 | −0.042 |
| 20 | 16.880 | 18.678 | 20.471 | 22.250 | 24.038 | 25.841 | 27.601 | 29.390 |
| | 16.945 | 18.730 | 20.515 | 22.300 | 24.084 | 25.869 | 27.654 | 29.439 |
| | −0.065 | −0.052 | −0.044 | −0.050 | −0.046 | −0.028 | −0.053 | −0.049 |
| 15 | .... | 22.492 | 25.036 | 27.578 | 30.120 | 32.639 | 35.194 | 37.713 |
| | .... | 22.473 | 25.010 | 27.547 | 30.084 | 32.622 | 35.159 | 37.696 |
| | .... | 0.019 | 0.026 | 0.031 | 0.036 | 0.017 | 0.035 | 0.017 |
| 12.5 | .... | 24.825 | 28.023 | 31.214 | 34.400 | 37.586 | 40.755 | 43.930 |
| | .... | 24.527 | 27.707 | 30.888 | 34.069 | 37.250 | 40.430 | 43.611 |
| | .... | 0.298 | 0.316 | 0.326 | 0.331 | 0.336 | 0.325 | 0.319 |
| 10 | .... | .... | 31.579 | 35.808 | 40.028 | 44.238 | 48.430 | 52.638 |
| | .... | .... | 30.029 | 34.220 | 38.412 | 42.603 | 46.795 | 50.986 |
| | .... | .... | 1.550 | 1.588 | 1.616 | 1.635 | 1.635 | 1.652 |

where the isometrics are substantially straight lines) the measured pressures are quite accurately reproduced, but at greater densities where presumably the molecular species of the substance is changing more rapidly, great discrepancies appear. It is hoped to consider this region in a later article.

## Accuracy Required of the Constants

It is perhaps of interest to discuss the error allowable in the constants of the equation in order to calculate the pressure to any desired accuracy.

$$\text{Since } \phi = \frac{A}{v^2}\, e^{-m/v}.$$

$$\Delta\phi = \frac{\phi}{A}\,\Delta A \qquad (1) \qquad\qquad \text{and} \qquad\qquad \Delta\phi = -\frac{\phi}{v}\,\Delta m \qquad (2)$$

$$\frac{\Delta\phi}{\phi} = \frac{\Delta A}{A} \qquad\qquad\qquad\qquad \frac{\Delta\phi}{\phi} = -\frac{\Delta m}{v}$$

$$\text{and since } \psi T = \frac{RT}{v-\delta}$$

$$\Delta(\psi T) = \frac{\psi T}{R}\,\Delta R \qquad (3) \qquad\qquad \text{and} \qquad\qquad \Delta(\psi T) = \frac{\psi T}{v-\delta}\,\Delta\delta$$

$$\frac{\Delta(\psi T)}{\psi T} = \frac{\Delta R}{R} \qquad\qquad\qquad\qquad \frac{\Delta(\psi T)}{\psi T} = \frac{\Delta\delta}{v-\delta}$$

Now $\delta = \beta e^{-\alpha/v}$, whence $\Delta\delta = e^{-\alpha/v}\Delta\beta - \beta/_v\, e^{-\alpha/v}\Delta\alpha$ from which we get by substitution in the equation above

$$\Delta(\psi T) = \frac{\psi T}{v-\delta} e^{-\alpha/v}\,\Delta\beta \qquad (4) \qquad\qquad \text{and} \qquad\qquad \Delta\psi T = -\frac{\psi T}{v-\delta}\,\frac{\delta}{v}\,\Delta\alpha \quad (5)$$

$$\frac{\Delta(\psi T)}{\psi T} = \frac{e^{-\alpha/v}}{v-\delta}\,\Delta\beta \qquad\qquad\qquad\qquad \frac{\Delta\psi T}{\psi T} = -\frac{\delta}{v(v-\delta)}\,\Delta\alpha$$

In Table VII are given the errors in each constant, which would cause an error of 0.01 atmosphere in the calculated pressure, for the two specific volumes 50 and 15 cc. per g. at 250°. The allowable error in each constant should be divided by 5 if it is required to know the pressure to 0.01 atmosphere.

Table VII

Errors in the Constants of the Equation of State Each Capable of Producing 0.01 Atmosphere Error in the Calculated Pressure

These divided by 5 give the allowable error which would produce a total error of 0.01 atmosphere in the pressure.

$t = 250$°C.

| | $v = 50$ cc./g. | | | $v = 15$ cc./g. | | |
|---|---|---|---|---|---|---|
| Constant | Value | Absolute error | Error % | Value | Absolute error | Error % |
| $R$ | 1.1074 | 0.00085 | 0.077 | 1.1074 | 0.00021 | 0.019 |
| $\beta$ | 5.9327 | .039 | .66 | 5.9327 | .0030 | .050 |
| $\alpha$ | 5.5815 | .33 | 5.8 | 5.5815 | .0075 | .14 |
| $A$ | 5709 | 26 | 0.45 | 5709 | 2.5 | .043 |
| $m$ | 1.468 | 0.23 | 15 | 1.468 | 0.0065 | .44 |
| $\delta$ | 5.306 | ... | .. | 4.089 | ... | .. |
| $\psi T$ | 12.96 | ... | .. | 53.092 | ... | .. |
| $\phi$ | 2.22 | ... | .. | 23.008 | ... | .. |
| $P$ | 10.74 | ... | .. | 30.084 | ... | .. |

## Summary

An apparatus for measuring the pressure-volume-temperature properties of gaseous substance with great accuracy has been described.

The isometrics of ethyl ether from a specific volume of 2.5 to 35 cc. per g. and from 175° to 325° have been measured. It was found that from 15 cc. per g. to the smallest densities the isometrics were substantially straight within the experimental error of the measurements. At densities greater than 15 cc. per g. the isometrics show a curvature which becomes greater as the density increases.

From the experimental data the Keyes equation of state for ether vapor was determined. This is $p = \frac{1.1074}{v-\delta} T - \frac{5709}{(v + 0.734)^2}$; $\log_{10} \delta = 0.77325 - \frac{2.4240}{v}$; $T = t°\text{C.} + 273.13$.

A modification of the last term of the Keyes equation, suggested by H. B. Phillips has been examined and found to hold as well as or slightly better than the original form. In this case the equation is $p = \frac{1.1074}{v-\delta} T - \frac{5709}{v^2} e^{-\frac{1.468}{v}}$ where $\log v^2\phi = 3.75656 - \frac{0.6375}{v}$, $\phi$ being the last term on the right hand side of the equation. In these equations $v$ is the specific volume in cc. per gram, and $p$ the pressure in atmospheres of 760 mm. of mercury at 0° and under standard conditions of gravitation.

The equation reproduces the measured pressures with great accuracy from the largest specific volumes to 15 cc. per g., that is, in the region of straight isometrics. At greater densities the equation in its present particular form cannot be used. The form which the equation takes in this region, where presumably the molecular species is changing (association or dissociation occurring) will be examined in a later article.

Cambridge 39, Massachusetts

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The Research Laboratory of Physical Chemistry

Serial No. 156 September, 1924

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# A CALORIMETER FOR MEASURING SPECIFIC HEATS AND HEATS OF VAPORIZATION OF LIQUIDS. THE SPECIFIC HEAT AND HEAT OF VAPORIZATION OF LIQUID ETHYL ETHER AT 0° AND 12°

by

Frederick G. Keyes and James A. Beattie

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# A CALORIMETER FOR MEASURING SPECIFIC HEATS AND HEATS OF VAPORIZATION OF LIQUIDS. THE SPECIFIC HEAT AND HEAT OF VAPORIZATION OF LIQUID ETHYL ETHER AT 0° AND 12°

By Frederick G. Keyes and James A. Beattie

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## Introduction

This investigation was carried out some years ago, and was concerned with the design of a calorimeter for the accurate determination of latent heats of vaporization of liquids, and of specific heats of liquids and compressed gases. The advantage of the apparatus is that it can be used over a wide series of temperatures, especially the range from room temperature down. The apparatus described in this article was used in determining some of the thermal properties of liquid ethyl ether at two temperatures below that of the room. With the aid of the experience so obtained the calorimeter has been redesigned and is being used for a study of the thermal properties of some other substances.

The usual method of determining specific heats is to place a known quantity of the substance in a calorimeter, to introduce a measured amount of energy, and to determine the rise in temperature. Corrections must be applied for the amount of energy absorbed by the calorimeter and for the various heat leakages, which often introduce great uncertainties into the result. Many special types of calorimeters have been designed to reduce or compensate one or both of these corrections for certain ranges of temperature, especially in the region near room temperature where thermostats can be accurately controlled.

The ordinary method of determining heats of vaporization of liquids is to draw off a measured portion of the dry saturated vapor, and determine the drop in temperature of the liquid remaining behind. The accuracy of the result is reduced by the many necessary corrections, as well as by any uncertainties in the specific heat of the liquid. In this field also, many special types of apparatus have been proposed and used.

## Previous Work

For the heat of vaporization of ethyl ether Regnault[1] gives the equation $r = 94.00 - 0.07901\,t - 0.0008514\,t^2$ and Winkelmann[2] from a recalculation of Regnault's results obtained the equation $r = 93.50 - 0.1082\,t - 0.0005033\,t^2$ where $t$ is the temperature in degrees centigrade, and $r$ the heat of vaporization in calories per gram.

Ramsay and Young,[3] substituting their measured values of specific volumes and vapor pressures in the Clapeyron equation, arrived at the value 93.27 calories per gram at 0° and 90.77 at 10°; and Mills[4] calculated 92.52 calories per gram at 0° and 87.54 at 20°.

As to the specific heat of liquid ether, the only values in the range from 0° to 12° are by Regnault,[5] whose data were represented by the equation $C = 0.529 + 0.000592\,t$, where $C$ is the specific heat of the liquid in calories per gram, along the saturation curve, and $t$ is the temperature in degrees centigrade. In Table I are given the values calculated from the above equations for the temperatures used in this investigation.

## The Apparatus

The apparatus consisted of a silver calorimeter enclosed in a glass vessel, so arranged that the space between could be evacuated when desired. Provision was made for withdrawing known amounts of dry saturated vapor at the temperature of the liquid, and for introducing measured quantities of electrical energy. The temperature of the liquid in the calorimeter was measured by means of a platinum thermometer placed in good thermal contact with it.

*The calorimeter* is shown in Fig. 1. A vessel A of silver 2 mm. thick, and 105 mm. long by 25 mm. in diameter, contained a re-entrant tube B, which reached almost to the bottom and enclosed a platinum thermometer. By means of a platinum ferrule this tube was connected to a glass tube, which carried the thermometer leads to the head C from which the usual connections were made to the temperature-measuring bridge, capable of indicating 0.0005°.

The tube carrying the thermometer leads was connected to the glass vacuum jacket by means of De Khotinsky cement. This vessel also possessed tubes for the introduction of the current wire and for the vapor exit tube, as well as a connection to a mercury diffusion pump for evacuation. This latter tube (not shown in the drawing) was of sufficient size, 1 cm. inside diameter, so that very high vacua could be quickly produced.

---

[1] Regnault, See Winkelmann, "Hand. d. Physik," J. H. Barth, Leipzig, **1906**, Vol. 3, p. 1093.

[2] Winkelmann, *Wied. Ann.*, **9,** 358 (1880).

[3] Ramsay and Young, *Phil. Trans.*, **178A,** 88 (1887).

[4] Mills, This Journal, **31,** 1123 (1909).

[5] Ref. 1, p. 196.

The vapor exit coil D was a silver tube 4.5 meters long and about 0.5 mm. inside diameter. It was doubly wound in the manner of a non-inductive resistance, one end projecting into a small cap E on the top of the calorimeter vessel, and the other passing out through the vacuum jacket to the volumenometer, a shut-off valve being in the line. (See also Fig. 2.) In order to leave the calorimeter, the vapor had to travel to the top of the cap, thence down through the tube to the bottom of the liquid and up again. By this means, it is believed that only dry saturated vapor at the temperature of the liquid was withdrawn. That part of the vapor tube which was outside of the calorimeter was much larger in diameter than the part inside.

The heating coil F consisted of an asbestos covered Nichrome wire drawn through a silver tube and soldered to it at the bottom end. The tube was soldered to the container and the wire projecting through was connected to a copper wire at K. The other electrical connection was made to the vapor-exit tube. The resistance of the heater was about 12 ohms.

The *accessory apparatus* is shown in Fig. 2. The calorimeter A was immersed in a bath at the desired temperature. The electrical current was furnished by a 3-cell lead storage battery E connected in parallel. In series with the battery were a standard resistance F, a variable resistance B, the heating coil of the calorimeter, and a switch D. Two leads from the standard resistance and two from the calorimeter were connected to the potentiometer J, through the double-throw double-pole switch G in such a manner that the potential drop across either could be measured. The voltage characteristics of the storage battery were studied with a view to determining the best time for using it. It was found that if after charging, it was allowed to discharge for several days through a resistance of about the same as that in the heating coil of the calorimeter. the voltage became very constant, changing less than one part in 300 during 24 hours.

The temperature was measured on the resistance bridge H.

The method of determining the amount of vapor distilled was to condense it into the volumenometer K, which consisted of a series of 5 calibrated bulbs, three of 1 cc. capacity and two of 10 cc., connected by calibrated capillary tubing. In making a determination of latent heat, this volumenometer was placed in a bath at a sufficiently low temperature to give the desired rate of distillation and the weight of ether distilled determined from its volume and independent measurements on the density.

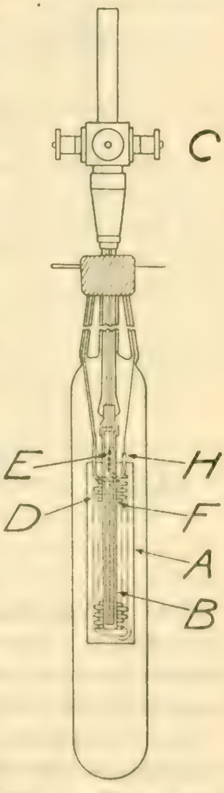

Fig. 1.—The calorimeter.

The *loading device* is also shown in Fig. 2. Because of the method used in determining the amount of ether distilled it was necessary to have no permanent gases present. The entire apparatus was evacuated until the pressure read less than 0.0001 mm. after standing. The glass tip from the tube N was broken under the surface of liquid ether which had been treated with sulfuric acid according to Willstätter's method, dried over calcium chloride and finally distilled over sodium to fresh sodium. The liquid was thus drawn into N. By the use of liquid ammonia it was distilled back and forth many times between the tubes M and N through a greaseless stopcock, the entire vapor phase being removed each time by evacuation. The removal of all the permanent gases was shown by the complete collapse of the vapor phase in the small inverted bell-shaped device under the hydrostatic pressure of the liquid. The stopcock L was opened and the liquid distilled into the volumenometer until full, the cock C being closed, and the loading apparatus sealed off at L. Before the final filling, the apparatus was rinsed out several times with ether vapor and evacuated to insure the complete removal of permanent gases. The amount of ether in the apparatus was thus known from the volume of liquid in the volumenometer, and the amount of vapor in the space above up to the cock C.

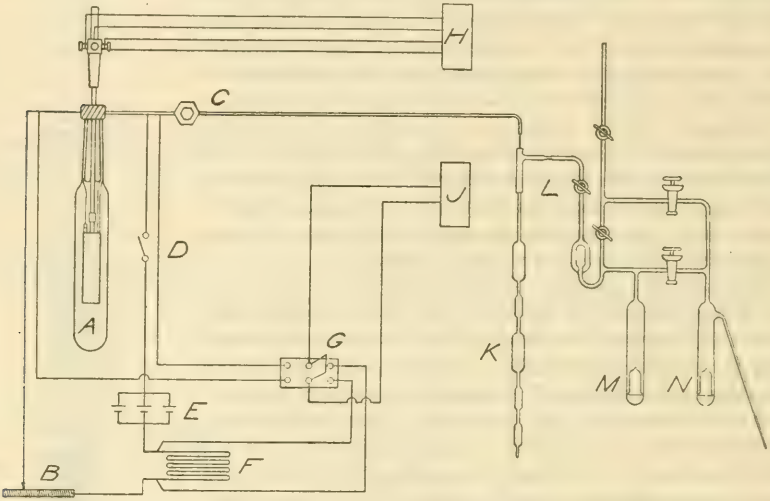

Fig. 2.—The accessory apparatus.

## Experimental Method

**Heat of Vaporization.**—The ether was distilled into the calorimeter by cooling it. The calorimeter was immersed in a thermostat at constant temperature and when the platinum thermometer indicated the same temperature as that of the bath, the glass jacket was evacuated.

The volumenometer was surrounded by a bath at a somewhat lower temperature than that of the calorimeter, using ice for the 12° run, and liquid ammonia for the 0° measurement, and cock C opened, thus causing the liquid to distil from the calorimeter. The sliding resistance in the battery circuit was so adjusted that the temperature indicated on the platinum thermometer remained constant, the temperature being read every minute. As the bulbs of the volumenometer filled, the bath around it was raised so that only the bulbs already filled, and that being filled, were cooled, thus preventing condensation in the bulbs above. As the meniscus passed along the capillaries between the bulbs, the time was read. It required about 30 minutes to fill one of the smaller bulbs, and four hours and a half for the larger.

During the filling of the first bulb no measurements were taken, since the current was being changed so as to keep the temperature in the calorimeter constant. After that only very small changes in the resistance were necessary. The energy input was determined by measuring the potential drops across the heating coil and standard resistance every two minutes and integrating with respect to the time the $EI$ products so obtained.

Two corrections were necessary to obtain the heat of vaporization from the amount of ether distilled, and the energy input. The first is applied to the weight of liquid evaporated and is due to the fact that the space occupied by the distilled liquid in the calorimeter at the beginning of a measurement was filled with vapor at the end; this can be calculated from the vapor density and the volume of the liquid distilled.

The second is caused by the Joule-Thomson cooling of the vapor due to the drop in pressure from the vapor pressure of the liquid in the calorimeter to that of the liquid in the volumenometer. Since the vapor tube outside the calorimeter was quite large and short, all this cooling was considered to have taken place in the calorimeter. The value of the Joule-Thomson coefficient $\mu$ was calculated from the Keyes equation of state for ether vapor. The heat withdrawn by $W$ grams of vapor dropping from a pressure of $p_1$ to $p_0$ is then, $Q = \mu\, C_p\, (p_1 - p_0)\, W$, assuming that $\mu$ and $C_p$ are constant over the pressure range $p_1$ to $p_0$.

This latter correction is due to the fact that it is the reversible heat of vaporization which is desired. The heat input measured in the calorimeter corresponds to an irreversible change, namely liquid ether at $t°$ converted into vapor at a pressure less than the vapor pressure at $t°$, the drop in pressure being carried out in the calorimeter by the vapor flowing through a fine tube. The irreversibility in the change in state is this latter process, and the correction can evidently be calculated by the Joule-Thomson coefficient as given above. The heat thus corrected is the reversible heat corresponding to the conversion of liquid ether at $t°$ to its vapor under the vapor pressure at $t°$.

The first of these two corrections amounts to about 0.1 calorie per gram, and the second, 0.15 calorie per gram at 0°, and although the latter could not be made with great accuracy (perhaps 10%), there were other factors which influenced the results more than the uncertainty in this correction.

**Specific Heat.**—Instead of measuring the heat capacity of the calorimeter empty and making a correction for it when determining the heat capacity of the liquid filling it, a procedure was employed which eliminated the necessity of such a measurement. All of the ether in the system was condensed into the calorimeter and a heat-capacity determination made, the cock C being closed. Then about half of the liquid was distilled into the volumenometer, the cock C closed and another determination made. In each case the exact weight of liquid in the calorimeter was known.

This gives two equations connecting the specific heat of ether and the heat capacity of the calorimeter, from which the latter could be eliminated.

The determinations were carried out in the ordinary manner. The calorimeter was placed in the thermostat and after taking readings of temperature for ten minutes the switch D was closed and the temperature read every half minute until the total rise was about 2°. The switch was then opened and the cooling curve followed for about 15 minutes. The energy input was determined by measuring the voltage drops across the heating coil and the standard resistance every minute and integrating, with respect to the time, the *EI* products so obtained.

In these measurements the temperature of the thermostat remained constant. However, the heating curve rose very steeply and was quite sharp at the top, indicating only a small heat leak.

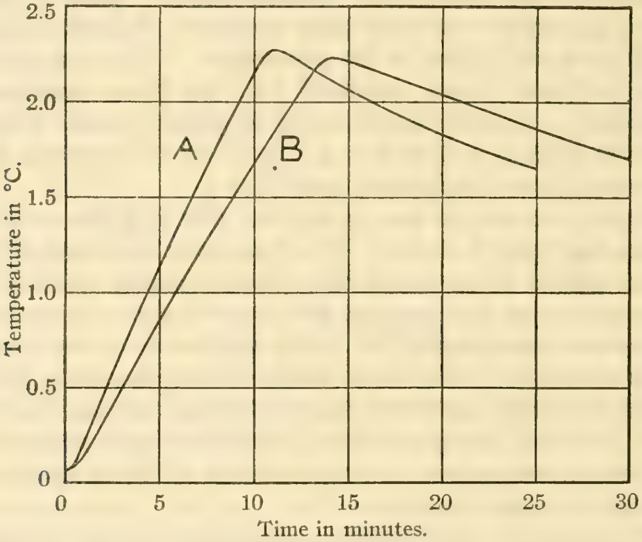

Fig. 3.—Heating curves for specific-heat determination. Curve A, Calorimeter half full. Curve B, Calorimeter full.

By raising the temperature of the thermostat at even approximately the same rate as that in the calorimeter, it is believed that the experimentally-determined temperature rise will require no correction.

There was, however, a temperature lag of from one half to one minute, due to the time required to transmit energy to the thermometer from the walls of its container. This can be greatly reduced by the use of platinum resistance thermometers of the flat type, for which the lag is practically zero.

A typical set of heating curves is shown in Fig. 3. The observed temperature increase was corrected for the radiation loss in the following manner. If $t_r$ is the radiation loss expressed in degrees and $\tau$ the time, then Newton's law of cooling gives $\frac{dt_r}{d\tau} = k\ (t-t_s) = k\ (f(\tau)-t_s)$, where $t$ is the temperature of the calorimeter at the time $\tau$, and is some function of $\tau$, and $t_s$ is the temperature of the thermostat. Integration gives $t_r = k\int_{\tau_1}^{\tau_2}[f(\tau) - t_s]\ d\tau = k \times$ (area under the heating curve) (Fig. 3). Now $k = \frac{dt_r}{d\tau}\left(\frac{1}{t-t_s}\right)$, and since the cooling curve at the end of the run is due to the loss of heat by radiation alone, the value of $k$ can be obtained from the slope of this line at any point, and its height above the initial temperature. This tangent can be accurately obtained since the cooling.curves are so nearly straight lines. The magnitude of this correction was about 0.3° on an observed temperature rise of 2.2°.

It will be noticed that at the beginning of a measurement the calorimeter was at the temperature of the thermostat so that no correction need be applied for the radiation loss at the start.

The energy input must be corrected for the small amount of vaporization which occurred due to the change in vapor pressure when the temperature was increased. In the case of the measurement with the calorimeter full, this was negligible.

## Results

In Tables I and II are given the results of the measurements taken in this investigation together with those of other observers. The references are given in an earlier paragraph.

TABLE I

HEAT OF VAPORIZATION OF ETHYL ETHER

Calories per gram

| Temp. °C. | Keyes and Beattie | Regnault | Winkelmann | Mills | Ramsay and Young |
|---|---|---|---|---|---|
| 0.1 | 90.50 | 93.99 | 93.49 | 92.52[a] | 93.27[a] |
| 11.8 | 88.83 | 92.95 | 92.15 | 87.54[b] | 90.77[c] |

[a] At 0°. [b] At 20°. [c] At 10°.

TABLE II

SPECIFIC HEAT OF LIQUID ETHYL ETHER

Calories per gram per degree

| Temp. °C. | Keyes and Beattie | Regnault |
|---|---|---|
| 1.2 | 568 | 530 |
| 13.4 | 577 | 537 |

## Accuracy of the Results

A comparison of the results of this investigation with those obtained by other observers shows that the present measurements lead to a higher value for the specific heat and a lower value of heat of vaporization than those measured by previous investigators.

An analysis of the various factors entering into the calculations of the specific heat and heat of vaporization leads to the conclusion that the probable accuracy of the present results is within about 1% in each case. By far the greatest factor entering into this uncertainty is that caused by the lag in the temperature measurement.

Further work is being carried out with a calorimeter of the same type as the one described in this investigation. It has been redesigned to permit the use of a platinum thermometer of the flat type, which the work of the present investigation indicated was very necessary in such a calorimeter, several other improvements being also incorporated.

## Summary

A new type of calorimeter for the determination of the specific heats and heats of vaporization of liquids is described. It can also be used for the determination of the specific heats of compressed gases. This calorimeter can be used over wide ranges of temperature and is especially suited for use in the range under room temperature.

The heat of vaporization and specific heat of liquid ethyl ether were determined for the temperatures 0° and 12°, with an accuracy within about 1%.

The main factor in reducing the accuracy of the results was determined, and the method of avoiding it given. Work is proceeding with the calorimeter in its improved form.

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# THE INFLUENCE OF GELATIN ON TRANSFERENCE NUMBERS

by

George Scatchard

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY,
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# THE INFLUENCE OF GELATIN ON TRANSFERENCE NUMBERS

BY GEORGE SCATCHARD[1]

RECEIVED FEBRUARY 18, 1924 PUBLISHED NOVEMBER 5, 1924

"The Influence of Gelatin on the Transference Numbers of Sulfuric Acid" by Ferguson and France[2] and "The Influence of Gelatin on the Transference Numbers of Hydrochloric Acid" by France and Moran[3] afford striking examples of the danger involved in the application of a physicochemical formula to conditions other than those of its derivation. Since these papers are of interest to biologists and others who cannot be expected to examine critically the validity of the formulas, it seems advisable to point out that the values which these authors give for transference numbers and for liquid-junction potentials cannot be interpreted as such quantities.

The formula used for the electromotive force of a concentration cell with transference is the ordinary one—for a uni-univalent electrolyte it is $E_- = t_+E = 2t_+ \frac{RT}{F} ln \frac{a_\pm'}{a_\pm}$, where $E_-$ is the electromotive force of a cell with transference with electrodes reversible to the anion, $E$ that of a cell without transference, $t_+$ is the transference number of the cation, and the $a_\pm$'s are the mean activities of the ions at the two concentrations.[4] It is derived through the assumption that, when an electric current passes through the cell, no matter is carried from one solution to the other except

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[1] National Research Fellow.

[2] Ferguson and France, THIS JOURNAL, **43**, 2161 (1921).

[3] France and Moran, *ibid.*, **46**, 19 (1924)

[4] The symbols of this paper are generally not the same as in the papers discussed. To facilitate comparison the following table is given.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| This paper | $E_-$ | $E_+$ | $E$ | $E_b$ | $E_x$ | $E_s$ | $t_+$ | $a$ |
| Ferguson, France and Moran | $E_{Cl}$, $E_{SO_4}$ | $E_H$ | $E$ | $E_b$ | $E_x$ | $E_s$ | $n_k$ | $C$ |

the ions under consideration. Whenever a second solute, such as gelatin, is present this assumption is contrary to fact because the water is certainly transferred and there will be changes in the concentration of the second solute which may lead to an appreciable error.[5]

In case the second solute is capable of producing ions, those ions will certainly be transferred, so that the error in the calculation of transference numbers may become enormous. From the work of other observers[6] there is little question but that gelatin and hydrochloric acid form a complex which ionizes largely to give chloride ion and a complex gelatin-hydrogen ion. Thermodynamically it makes no difference, of course, whether the mechanism of the reaction is as described or the gelatin reacts with the hydrogen ion to form a complex ion, a part of which combines with the chloride ion.

The cell will be still more complicated and different from the simple one postulated in the derivation of the formula if the concentration of the second electrolyte varies in the different parts of the cell. Such are the cells described in these papers. An example is,

$$\text{Pt, H}_2|\text{HCl }(0.1\ M)\underset{a_{\pm}'\ \ \overrightarrow{E_x}\ \ a_{\pm}''}{|}\text{HCl }(0.1\ M),\text{ gel }(c)\underset{\overrightarrow{E_b}\ \ a_{\pm}'''}{|}\text{HCl }(0.01\ M),\text{ gel }(c)\underset{\overleftarrow{E_z}\ \ a_{\pm}}{|}\text{HCl }(0.01\ M)|\text{H}_2\text{,Pt} \quad (1)$$

Taking into account the chemical reaction, this becomes:

$$\text{Pt, H}_2|\text{HCl }(0.1\ M)|\text{HCl }(0.1\ M-x),\text{ GelCl }(x),\text{ gel }(c-x)|\text{HCl }(0.01\ M-z),\text{ GelCl }(z)\text{ gel }(c-z)|\text{HCl }(0.01\ M)|\text{H}_2\text{, Pt} \quad (1')$$

where $z$ is either slightly less than $x$ or slightly less than 0.01 $M$. Perhaps the discussion will be clearer if we set up an analogous cell entirely of inorganic solutes, neglecting the unchanged gelatin even though its effect must be greater than that of the neutral solute mentioned in the second paragraph because its concentration is different in the different parts of the cell. Such a cell would be,

$$\text{Pt, H}_2\ |\ \text{HCl }(0.1\ M)\ |\ \text{HCl }(0.1\ M-x),\text{ LiCl }(x)\ |\ \text{HCl }(0.01\ M-z),\text{ LiCl }(z)\ |\ \text{HCl }(0.01\ M)\ |\ \text{H}_2\text{, Pt} \quad (2)$$

From inspection of these cells it is obvious that when an electric current passes through there must be a transfer of the ions of both the acid and the salt through all three of the liquid junctions, and that the mean activity of the ions of hydrochloric acid is not the same in either one of the end solutions as in the corresponding middle solution. The formula which assumes the same activities at the electrodes as at the middle liquid junction *(b)* and that the only transfer is that of the ions of hydrochloric acid across this junction is certainly not applicable. The cell is far too complicated to be interpreted from our present knowledge. Whatever the ratio of its electromotive force to that of a concentration cell without transference may be, it is not a transference number.

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[5] I have already pointed out this danger in a previous paper [(a) THIS JOURNAL, **45,** 1719 (1923)]. I noted there that this formula had never been derived rigorously. Dr. R. H. Gerke has called my attention to the fact that the derivation of Lewis and Randall [(b) "Thermodynamics," McGraw-Hill Book Co., **1923,** p. 337] becomes rigorous if the differential elements are defined, not to have constant volume, but to contain constant amounts of water, and the transference number is defined in terms of molalities rather than concentrations. This latter definition is consistent with recent experimental practise. My previous statement must now be withdrawn for the case of a solution of a single electrolyte. When a second solute is present, however, any movement of the water relative to the ordinary space coördinates would appear as a movement of the solutes relative to these special coördinates, and the difficulty remains.

[6] J. Loeb, "Proteins and the Theory of Colloid Behavior," McGraw-Hill Book Co., **1922,** Chap. V. D. I. Hitchcock, *J. Gen. Physiol.,* **4,** 733 (1922); **5,** 383; **6,** 95, 201 (1923).

The authors justify the omission of gelatin from the electrode solutions by the statement, "the influence of gelatin on transference is due only to its effect on the boundary potential."[7] In the next paragraph, however, they describe difficulties due to the diffusion of the gelatin to the electrodes. Later[8] they give values for the electromotive force of the cell, $H_2$,Pt | HCl (0.1 *M*) | KCl (*M*) | HCl (0.1 *M*), gel (*c*) | $H_2$,Pt, which show an effect of the gelatin many times larger than a possible error in the assumption that the potassium chloride bridge eliminates liquid-junction potentials. In the paper of France and Moran the concentrations of hydrogen ion are calculated from the formula, $E' = 2RT/F \ ln \ a'_+/a_+$ instead of $E' = RT/F \ ln \ a'_+/a_+$, so that their calculated change in concentration is much too small. The values calculated from their measurements are given in Table I, in which the values for the solutions without gelatin are taken from their paper. It is clear that, unless the liquid-junction potential with potassium chloride changes enormously, the gelatin does have an important effect on the potential drop at the hydrogen electrode, and that the results would be quite different if gelatin were present in the electrode solutions.

TABLE I

CELLS WITH HYDROGEN ELECTRODE AND POTASSIUM CHLORIDE BRIDGE

| Gelatin | 0.1 *M* | | 0.01 *M* | |
|---|---|---|---|---|
| % | $E'$ | $a_+$ | $E'$ | $a_+$ |
| 0 | ..... | 0.0917 | ..... | 0.00975 |
| 1 | 0.00217 | .0843 | 0.03946 | .00210 |
| 2 | .00391 | .0788 | .09754 | .00022 |
| 3 | .00588 | .0729 | .12057 | .00009 |
| 4 | .00789 | .0674 | .12421 | .00008 |

The customary formula for the liquid-junction potential in a concentration cell is for uni-univalent electrolytes: $E_b = (1-2t_-) \frac{RT}{F} \ ln \ \frac{a_\pm'}{a_\pm} = \frac{(1-2t_-)}{2} E = \frac{E_- - E_+}{2}$ where $E_b$ is the liquid-junction potential. The first form is derived by subtracting the electrode potentials from the total electromotive force of the cell with transference; the others, by combining the first with the formulas for the total electromotive force of the various cells. They depend upon the same assumptions as the formula for the electromotive force of the cell with transference. Moreover, the electrode potentials are calculated on the assumption that in any solution the positive and negative ions have equal activities. This assumption is contrary to present day theories of the nature of electrolytic solutions. Probably the error is small for solutions of 0.1 and 0.01 *M* hydrochloric acid; it is 1.6 millivolt according to the values given by Lewis and Randall.[9] For sulfuric acid it may be somewhat larger. Moreover, it is obvious from inspection of the type cells given above that there are three liquid-junction potentials. The value given by the authors for the liquid-junction potential would be the sum of the three potentials if the assumptions were justified. All that can be obtained from these measurements without assumption is that the change in the total electromotive force on the addition of gelatin equals the sum of these three potentials minus the single liquid-junction potential when no gelatin is present.

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[7] Ref. 2, p. 2162

[8] Tables IV in both papers.

Planck[10] and Henderson[11] have derived formulas for the potential at liquid junctions of this type, using two different assumptions as to the nature of the junction. They both assume that ionization is complete and that both the activity coefficients and the mobilities are independent of the concentration. The first assumption is incompatible with each of the other two for solutions of finite concentration, so that the formulas are certainly not accurate. Moreover, they require a knowledge of the concentration and mobility of each ion, so that they are not applicable to the present case even as approximations.

The papers of Ferguson, France and Moran also include a supposed proof that the change in liquid-junction potential cannot be due to a change in acid concentration because the algebraic sum of the three liquid-junction potentials, calculated on the assumption that the activity of the chloride ion is equal to that of the hydrogen ion as measured by the cell with potassium chloride bridge, is equal to the potential when no gelatin is present ($E_0$). The symbols for these potentials and for the activities in the four solutions are indicated in the first cell diagram (1). The check equation is $E_x + E_b - E_z = E_0$ or $E_z - E_x = E_b - E_0$. The formulas for the potentials used by the authors are,

$$E_z = [(1-2t_-)RT/F](ln\ a_{\pm} - ln\ a_{\pm}''') \quad E_x = [(1-2t_-)RT/F](ln\ a_{\pm}' - ln\ a_{\pm}'')$$

$$E_b = [(1-2t_-)RT/F](ln\ a_{\pm}'' - ln\ a_{\pm}''') \quad E_0 = [(1-2t_-)RT/F](ln\ a_{\pm}' - ln\ a_{\pm})$$

Obviously $E_z - E_x = E_b - E_0 = [(1-2i_-)RT/F](ln\ a_{\pm} - ln\ a_{\pm}''' + ln\ a_{\pm}'' - ln\ a_{\pm}')$, and this equation must hold whatever values are given to the transference number and to the activities in the different solutions.

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[9] Ref. 5 b, p. 382.

[10] Planck, *Ann. Physik*, **40**, 561 (1890).

[11] Henderson, *Z. physik. Chem.*, **59**, 117 (1907); **63**, 325 (1908).

The small discrepancies found by the authors must be due to inaccuracies in calculation rather than to slight experimental errors.

It is clear that this proof does not depend at all upon experiment. As a mathematical argument, it merely proves that, in a concentration cell containing but one solute, the electromotive force depends only on the concentrations at the electrodes, and not at all upon intermediate concentrations. This has been proved many times in the literature. Perhaps the simplest proof is that of Lewis and Randall.[5b]

It may be added that, even if the transference numbers and liquid-junction potentials were correct as given, there would be nothing in these papers which appears to me to be evidence bearing on any of the following questions which the authors discuss: Is the reaction of gelatin and hydrochloric acid a stoichiometrical chemical reaction or an adsorption? Is there a single compound, or several? Is the reaction one between gelatin and hydrochloric acid, or between gelatin and hydrogen ion? There does appear to be evidence in the work of others referred to above[6] that the authors' conclusions regarding the first two are correct.

## Summary

1. The values given by Ferguson and France and by France and Moran for the transference numbers of sulfuric and hydrochloric acids in the presence of gelatin and for the liquid-junction potentials in concentration cells of these acids containing gelatin cannot be so interpreted.

2. The cells measured by these authors are too complicated for interpretation without supplementary experiments and without an extension of the theory of liquid junctions.

3. Their proof that the change in liquid-junction potential is not produced by a change in acid concentration is independent of the experimental measurements upon which it is apparently based.

4. The experimental results, however interpreted, do not give evidence either for or against many of the conclusions drawn by the authors.

Cambridge A, Massachusetts

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# EVIDENCE OF ASSOCIATION IN CARBON DIOXIDE FROM THE JOULE-THOMSON EFFECT

by

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# EVIDENCE OF ASSOCIATION IN CARBON DIOXIDE FROM THE JOULE-THOMSON EFFECT

BY FREDERICK G. KEYES

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## Introduction

There has recently appeared an important paper by Burnett[1] dealing with the experimental determination of the Joule-Thomson effect for carbon dioxide. The measurements extend from about —24° to 120° in temperature and cover a pressure range of 20 to 75 atmospheres. By means of empirical equations these data, together with the data of Jenkins and Pye,[2] have been correlated by Burnett and yield values of the Joule-Thomson effect at temperatures from 220°K. to 400°K. for the constant pressure of one atmosphere. These values have been selected for the present contribution to the theory of the Joule-Thomson effect since at low pressures the effect tends to become a function of the temperature alone.

In a previous paper dealing with the Joule-Thomson effect for air[3] it was shown that the pressure-volume-temperature data of all observers were in conformity with the measurements existing for the Joule-Thomson effect for air as well as with the specific-heat data for air.

In the case of carbon dioxide the $p,v,T$ data due to Andrews as corrected by Ramsay[4] have been shown[5] to indicate that for the range of the experiments the pressure-temperature relation at constant volume is linear. The constant-volume specific-heat measurements of Joly,[6] for carbon dioxide, however, indicate that the pressure is not linear with temperature at constant volume. The work of Burnett which supplies Joule-Thomson data also indicates that the constant-volume pressures are not strictly linear with temperature.

The data have heretofore not been available[7] for examining to what extent the assumption of association in a gas may be of service in providing an explanation of certain apparent inconsistencies in the general properties of a fluid. For example, the linearity of the constant-volume increase of pressure with temperature in the case of carbon dioxide is, as has been stated, at variance, in the inferences deduced therefrom, with the Joly specific-heat measurements and with the recent Joule-Thomson measurements of Burnett. It was foreseen a number of years ago that the existence of a very small fraction of polymerized molecules could exercise a pronounced influence on both the specific heats and the Joule-Thomson effect and yet hardly be detectable from measurements of $p$, $v$ and $T$.

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[1] Burnett, *Phys. Rev.*, **22,** 590 (1923).

[2] Jenkins and Pye, *Phil. Trans.*, **213A,** 67 (1914); **214A,** 353 (1915).

[3] THIS JOURNAL, **43,** 1452 (1921).

[4] Ramsay, *Z. physik. Chem.*, **1,** 433 (1887).

[5] *J. Am. Soc. Ref. Engineers*, **3,** 17 (1917).

[6] Joly, *Proc. Roy. Soc.* (London), **41,** 352 (1886); *Phil. Trans.*, **182A,** 73 (1891); **185A,** 943 (1894).

[7] The recent specific-heat data of the Bureau of Standards for ammonia furnish additional data for examining further the validity of the ideas presented in this paper.

## Theoretical Treatment

The Andrews data for carbon dioxide have been shown to be represented[8] by the equation of state of form (see Table I)

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v + l)^2} \tag{1}$$

TABLE I

ANDREWS' DATA FOR CARBON DIOXIDE COMPARED WITH PRESSURES COMPUTED BY EQUATION OF STATE

| Temp. | 30 cc. | | 25 cc. | | 20 cc. | | 15 cc. | |
|---|---|---|---|---|---|---|---|---|
| °C. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. | Calc. |
| 0.0 | 15.074 | 15.102 | 17.695 | 17.690 | 21.224 | 21.333 | 26.670 | 26.723 |
| 6.1 | 15.488 | 15.503 | 18.200 | 18.192 | 21.871 | 21.979 | 27.573 | 27.627 |
| 31.1 | 17.221 | 17.232 | 20.315 | 20.295 | 24.579 | 24.683 | 31.355 | 31.407 |
| 48.1 | 18.396 | 18.396 | 21.745 | 21.719 | 26.413 | 26.515 | 33.916 | 33.968 |
| 64.0 | 19.495 | 19.484 | 23.084 | 23.051 | 28.129 | 28.228 | 36.312 | 36.363 |
| 100.0 | 21.982 | 21.950 | 26.116 | 26.066 | 32.013 | 32.107 | 41.736 | 41.785 |

Pressures in atms. of 76 cm. of Hg; vol. in cc. per gram.

$$p = \frac{1.865}{v - \delta} T - \frac{3219}{(v - 0.055)^2};\ \log_{10}\delta = 0.4650 - \frac{0.7065}{v}$$

This equation was deduced[9] for an unchanging or constant molecular species. Table I indicates the degree of approximation with which it reproduces the Andrews data and the agreement is believed to be all that may be expected. If polymerization exists it must be judged to be small in amount and incapable of exercising appreciable influence on the accuracy of the constants of the equation.

Assuming therefore that the constants of the equation are relatively accurate, the equation to be used in examining the effect of the presence of a small fraction of double molecules may be obtained by applying for the calculation of derived quantities the equation,

$$p = \frac{R(1 - y/2)T}{v - \delta} - \frac{A}{(v + l)^2} \tag{2}$$

Since this equation is to be used for low pressures it will suffice if $\alpha$ and $l$ are considered negligible and there results

$$p = \frac{R(1 - y/2)T}{v - \beta} - \frac{A}{v^2} \tag{3}$$

The fraction associated, $y$, is in this instance considered to be so small as not to affect the values of $\beta$ or $A$. There is evidence to show that $\beta$

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[8] Ref. 4, p. 445.

[9] *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

for any value of $y$ is $\beta(1-y/2)$. In the case of carbon dioxide on the other hand, at one atmosphere and 0° $\beta$ is required to be known with an accuracy of only 3% for pressures to one part in 5000. A value of 0.001 for $y$ would, therefore, be negligible. A similar statement may be made with regard to $A$. The fraction associated enters, therefore, at low pressures only through the term $R(1-y/2)$.

Forming the derivative $\left(\frac{\partial v}{\partial T}\right)_p$ from (3) there results,

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{v-\beta}{T} \quad \frac{1 - \dfrac{T}{2(1-y/2)}\left(\dfrac{\partial y}{\partial T}\right)_p}{1 - \dfrac{2A}{RT}\dfrac{(v-\beta)^2}{v^3}\dfrac{1}{1-y/2}} = \frac{v-\beta}{T} \quad \frac{1 - \dfrac{T}{2}\left(\dfrac{\partial y}{\partial T}\right)_p}{1 - \dfrac{2A}{RT}\dfrac{(v-B)^2}{v^3}} \tag{4}$$

When Equation 4 is substituted in the general thermodynamic equation for the Joule-Thomson effect where $\omega$ represents $v-\beta$ there results

$$C_p\mu = C_p\frac{\mathrm{d}T}{\mathrm{d}p} = T\left(\frac{\partial v}{\partial T}\right)_p - v = \frac{2A}{RT}\left(\frac{\omega}{v}\right)^2 - \beta - \frac{\omega T}{2}\left(\frac{\partial y}{\partial T}\right)_p$$

Considering $\left(\frac{\omega}{v}\right)^2$ as substantially equal to unity and assuming $\omega = v$ in $\frac{\omega T}{2}\left(\frac{\partial y}{\partial T}\right)_p$ the equation becomes

$$\mu C_p = \frac{2A}{RT} - \beta - \frac{vT}{2}\left(\frac{\partial y}{\partial T}\right)_p \tag{5}$$

The application of thermodynamics to a gaseous reaction of the type, $CO_2 = {}^1/_2(CO_2)_2$, leads to the following equation where $y$ is small and $C$ a constant, $\Delta U^0$ being the heat of reaction at absolute zero for one mole or 44 g. of carbon dioxide:

$$y = C\,e^{\frac{2\Delta U^0}{RT}}\frac{R}{v}\frac{1}{T^{3/2}} = C\,e^{\frac{2\Delta U^0}{RT}}\frac{p}{T^{5/2}} \tag{6}$$

From this equation there results, where $\Delta H_p$ is the heat of reaction at $T$ and constant pressure,

$$\left(\frac{\partial y}{\partial T}\right)_p = -2y\frac{\Delta H_p}{RT^2} \tag{7}$$

Substituting in (5) gives, where $C_p\mu_0$ represents $\frac{2A}{RT} - \beta$ and $v$ is taken to be equivalent to $\frac{RT}{p}$

$$C_p\mu = C_p\mu_0 + \frac{y}{p}\Delta H_p \tag{8}$$

From Equation 6, $y$ is seen to vary as the pressure, and since $\Delta H_p$ is a function of the temperature alone it is clear that the effect of the term, $\frac{y}{p}\Delta H_p$, diminishes with temperature increase, but is independent of the pressure. It appears then that the Joule-Thomson effect, in a gas containing a small fraction of associated molecules, consists of the normal effect due to the deviation from the perfect gas laws for the single molecular species, to which must be added a change in temperature with pressure due to a small shift in the molecular species.

This is an important conclusion, if true, since it provides a means of obtaining the constants of the association Equation 6 which should enable values of the pressure coefficient of the specific heat at constant volume to be calculated and these latter are very much affected where the association is appreciable because of the large value of $\Delta H_p$ as compared with the small value of the heat capacity of the unassociated molecules *per se*. Conversely, it is important to be able to obtain, from the measurements at definite pressures and various temperatures of the apparent specific-heat capacities of gases, the heat capacities of single species types of molecules. Indeed, until this is possible little progress can be made in the development of a sound theory of the dependence of internal energy of single molecular species on temperature.

Substituting the value of $y$ from (6) in Equation 8 there results

$$C_p\mu = \frac{2A}{RT} - \beta + \frac{C\,e^{\frac{2\Delta U_0}{RT}}}{T^{5/2}}\,\Delta H_p \tag{9}$$

In this equation $C_p\mu$ represents the product of the measured value of the Joule-Thomson effect with the specific heat at the pressure to which the effect corresponds. Evidently at high temperature $C_p\mu$ considered as a function of $1/T$ would be expected to approach linearity since the third term of the right hand member becomes evanescent. Air, for example, at temperatures above zero (and at one atmosphere) gives values of $C_p\mu$ which are linear in $1/T$, and values at low temperatures (—100°) would be most interesting to supplement the measurements above zero.

## The Numerical Data

The results obtained by Burnett for the Joule-Thomson effect at one atmosphere and temperatures from 220°K. to 400°K. have been multiplied by the value of $C_p$ at one atmosphere corresponding to the temperature for each datum.

The equation of state constants have also been used to compute for the round temperatures from 220° to 400° the value of $\mu C_p$ or $\frac{2A}{RT} - \beta$. By subtracting the latter from $\mu C_p$, the Burnett Joule-Thomson coefficients for carbon dioxide multiplied by the constant-pressure heat capacity per mole in cc./atm., there remains the last term of (8) or $\frac{y}{p}\Delta H_p$ for the one atmosphere pressure.

It is clear that if the logarithms of these differences increased by $\frac{5}{2}\log T$

and denoted by $\log(\Delta\mu C_p T^{5/2})$ are used to construct a rectangular diagram with $1/T$ a straight line should result, the slope of which is approximately $2\Delta U^0/2.3R$ and the intercept of value $(\log C + \log \Delta H_p)$. The latter quantity is of course not constant, because $\Delta H_p$ is a function of the temperature, $\Delta H_p = \Delta U^0 + \frac{5}{4}RT$. However, since the slope gives the approximate value of $\Delta U^0$ or therefrom $\Delta H_p$, a second plotting of $\log \frac{\Delta\mu C_p T^{5/2}}{\Delta H_p}$ and $\frac{1}{T}$ will give the true value of $\Delta U^0$ and the constant $C$ in the dissociation equation based on the assumption that the difference in the specific heats of one mole of $CO_2$ and $^1/_2$ mole of $(CO_2)_2$ is $^3/_4 R$ independent of temperature. This latter assumption is not exactly correct but the resulting approximation is the best compromise in the present state of our knowledge of the specific heats of gases.

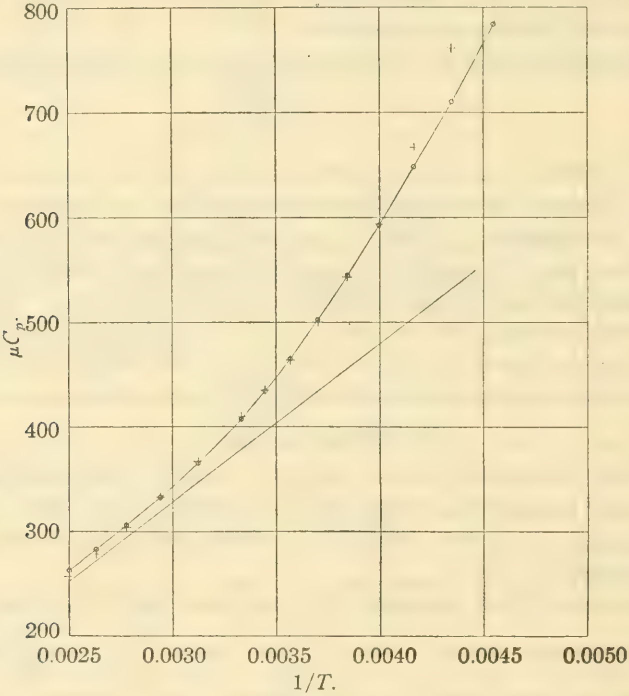

Fig. 1.

In Fig. 1 there are represented the measured values of $\mu C_p$, the $\mu_0 C_p$ computed from the equation of state and corresponding to $y = 0$, and in Fig. 2, $\log \frac{\Delta\mu C_p T^{5/2}}{\Delta H_p}$, all of which quantities are plotted with $1/T$ as independent variable. The latter data for the temperatures —53°, —43° and

—33° are seen to tend away from the straight line drawn through the majority of the data. These are data which are extrapolated from the values at higher temperatures and in any case should be measured with particular care since the physical assumption underlying the whole of the present thought is that equilibrium among the single and double molecules is instantaneously attained in the Joule-Thomson measurements. The coördinates corresponding to the highest temperatures are obtained as the differences between large numbers and cannot be expected to correlate exactly with the data more favorably computed.[10]

It is of interest to compute the $\mu C_p$ values using the equation of state together with the equation for the association now obtained. The crosses in the diagram represent the computed values and Burnett's curve is seen to be very well represented with the exception of the three lowest temperature points.

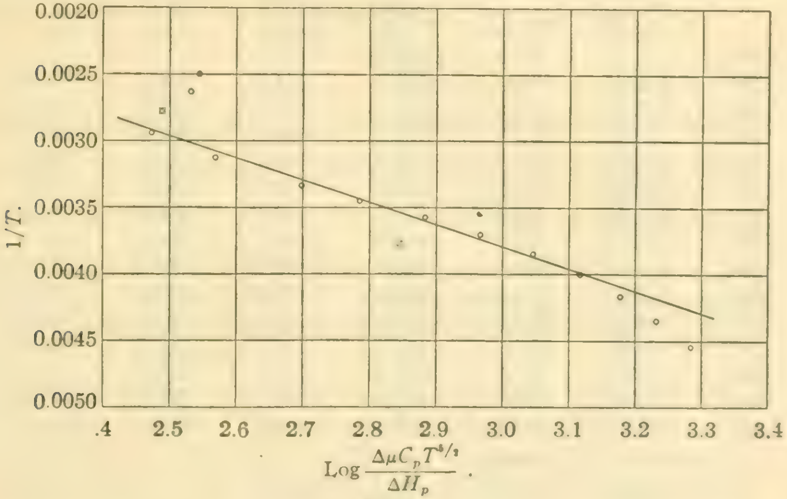

Fig. 2.

Table II presents all the data employed together with the values of $y$ corresponding to each temperature. Col. 12 gives the computed $\mu$ values corresponding to the crosses in the diagram.

The values of $y$ are seen to be very small corresponding to 1 double molecule in 500 at —53° and 1 in 20,000 at 127°. The values are undoubtedly only approximate since the $\beta$ and $A$ constants of the carbon dioxide molecules are not final but to be regarded as tentative until new $p,v,T$ data are available. The Burnett curve is seen to be straightening out at high temperatures with a slope close to that of the equation of state line corresponding to no association. This is as it should be if associated molecules really are a factor in the Joule-Thomson effect.

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[10] The equation for log $y$ is: $\log_{10} y = 0.715 + \frac{603}{T} - 5/2 \log_{10} T + \log_{10} p$.

### The Constant-Volume Specific Heat

Joly, employing his steam calorimeter for measuring the constant-volume specific heat of carbon dioxide, obtained data which he represented by the following equation where $\rho$ is the density: $C_v = 0.1650 + 0.2125\rho + 0.3400\rho^2$. This equation refers to the average temperature between 16° and 100°.

TABLE II

NUMERICAL DATA AND STEPS IN THE CALCULATIONS

| $T$ | Obs. $\mu^{\text{deg.}}/_{\text{atm.}}$ Burnett | $C_p{}^{\text{cal.}}/_{\text{mole}}$ | $C_p \frac{\text{cc. atm.}}{\text{mole}}$ | Obs. $\mu C_p$ Burnett | Calcd. $\mu_0 C_p$ Eq. state | $\Delta\mu C_p$ obs. |
|---|---|---|---|---|---|---|
| 200 | .... | 8.10 | 334.5 | ... | ... | ... |
| 220 | 2.3035 | 8.24 | 340.3 | 784.0 | 562.0 | 177.6 |
| 230 | 2.0700 | 8.31 | 343.1 | 710.2 | 532.0 | 178.2 |
| 240 | 1.8700 | 8.39 | 346.5 | 648.0 | 504.6 | 143.4 |
| 250 | 1.6954 | 8.48 | 350.0 | 593.0 | 479.2 | 113.8 |
| 260 | 1.5405 | 8.56 | 353.5 | 544.6 | 456.0 | 88.6 |
| 270 | 1.4060 | 8.65 | 357.2 | 502.2 | 434.2 | 68.0 |
| 280 | 1.2900 | 8.74 | 361.0 | 465.7 | 413.8 | 51.9 |
| 290 | 1.1900 | 8.83 | 364.7 | 434.0 | 395.7 | 38.3 |
| 300 | 1.1045 | 8.93 | 368.8 | 407.2 | 378.0 | 29.2 |
| 320 | 0.9665 | 9.15 | 377.9 | 365.2 | 346.3 | 18.9 |
| 340 | .8595 | 9.35 | 386.2 | 332.0 | 318.7 | 13.3 |
| 360 | .7750 | 9.55 | 394.2 | 305.7 | 293.5 | 12.2 |
| 380 | .7045 | 9.73 | 401.8 | 283.1 | 271.1 | 12.0 |
| 400 | .6440 | 9.89 | 407.5 | 262.4 | 251.3 | 11.1 |

| $T$ | $\text{Log}_{10}$ $\Delta\mu C_p T^{5/2}$ | $\text{Log}_{10}$ $\frac{\Delta\mu C_p T^{5/2}}{\Delta H_p}$ | $\frac{10^4}{T}$ | Calcd. $\Delta\mu C_p$ | Calcd. $\mu$ | $y$ |
|---|---|---|---|---|---|---|
| 200 | ..... | ..... | ... | ... | ... | ...... |
| 220 | 8.10549 | 3.18668 | 45.45 | 329.8 | 2.623 | 0.0040 |
| 230 | 8.15524 | 3.25106 | 43.48 | 229.0 | 2.219 | .0027 |
| 240 | 8.10708 | 3.17759 | 41.67 | 162.0 | 1.925 | .0019 |
| 250 | 8.05099 | 3.11626 | 40.00 | 116.6 | 1.702 | .0014 |
| 260 | 7.98486 | 3.04516 | 38.46 | 87.1 | 1.536 | .0010 |
| 270 | 7.91091 | 2.96589 | 37.04 | 65.9 | 1.400 | .00075 |
| 280 | 7.83307 | 2.88319 | 35.71 | 50.5 | 1.286 | .00057 |
| 290 | 7.73920 | 2.78412 | 34.48 | 39.4 | 1.193 | .00045 |
| 300 | 7.65818 | 2.69835 | 33.33 | 31.1 | 1.110 | .00034 |
| 320 | 7.53734 | 2.56875 | 31.25 | 20.3 | 0.970 | .00023 |
| 340 | 7.45255 | 2.47348 | 29.41 | 13.8 | .860 | .00014 |
| 360 | 7.47711 | 2.48892 | 27.78 | 9.7 | .769 | .00010 |
| 380 | 7.52863 | 2.53150 | 26.31 | 7.1 | .692 | .000071 |
| 400 | 7.55047 | 2.54441 | 25.00 | 5.3 | .630 | .000052 |

From the study of substances in the gaseous phase carried out in this Laboratory the conclusion at present is that for a single molecular species the pressure is strictly a linear function of the temperature. This implies directly that the constant-volume specific heat for a single molecular species depends on the temperature alone. This is a most important fact to ascertain and specific heat measurements made preferably at constant volume are now most urgently needed to provide a more precise insight into the properties of single molecular species. The Joule-Thomson data for carbon dioxide appear to substantiate the view that association in carbon dioxide actually exists and the equation for the fraction associated ($y$) may be used to compute the coefficient of the density for the specific heat between 16° and 100°.

A measured value of $C_v$ for a fluid containing a small fraction of associated molecules would be, where $C_v^0$ is the value for $y = 0$,

$$C_v = C_v^0 + \Delta H_v \left(\frac{\partial y}{\partial T}\right)_v \tag{12}$$

In this equation $\left(\frac{\partial y}{\partial T}\right)_v$ must be computed as the mean value between 16° and 100° to correspond with the temperature interval employed by Joly. There is obtained $2.2 \times 10^{-3} \frac{1}{v}$. The heat of the reaction at constant volume for the temperature interval is 1880 cal. per mole or 44.7 cal. per g. The coefficient of $1/v$ or the density becomes, therefore, 0.094, and the constant-volume specific heat equation as far as the first term is, $C_v = C_v^0 + 0.094\rho$.

The coefficient is seen to be 0.094 as compared with 0.2125 of Joly or nearly $2\frac{1}{2}$ times smaller. The agreement is not good and further work alone can resolve the discrepancy. Several comments are, however, at the moment apropos. The Joule-Thomson coefficient is necessarily obtained from measurements on a fluid in rapid motion. Equation 5, on the other hand, is deduced on the assumption that true chemical equilibrium exists at every instant of the measurement. It is, however, a well-known fact that in general a chemical reaction possesses a finite velocity increasing with rising temperature, which would preclude instantaneous adjustment. In the case of associating nitrogen dioxide, however, the adjustment of the single and double species is known to take place very rapidly. In any event until it can be assured that the equilibrium can actually adjust itself with sufficient rapidity the measurement of the Joule-Thomson effect for an associating gas presents peculiar difficulties.[11]

The specific heat measurement at constant volume is an experimental problem of particular difficulty. The copper spheres used by Joly required numerous corrections, one of which was briefly discussed in the paper on the Joule-Thomson effect for air. This is the change in heat capacity of the metal of the sphere due to tension produced by the gas inclosed. In addition to this effect there is also the heat due to stretching of the metal walls as the gas heats from 16° to 100°. Joly mentions this effect but dismisses it as of small magnitude. Another effect which may attain a magnitude sufficient to require consideration is the adsorption on the container walls and its shift with change in temperature. Heats of adsorption are enormous as compared with the heat capacity and, should such an effect exist, it would give a decided trend to the measured heat capacities.

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[11] Professor A. B. Lamb, in conversation, made the very pertinent suggestion that experiments might be made with Joule Thomson plugs in which catalysts were present, thus submitting to direct test the question of equilibrium attainment.

## Summary

1. The equation for the Joule-Thomson effect is deduced for a gas containing a small fraction of associated molecules. The deduction is based on the assumption that true chemical equilibrium exists at every stage of the effect.

2. The equation is compared with the recent Joule-Thomson data of Burnett for one atmosphere and qualitatively found to be in agreement. Quantitatively, the fraction associated deduced from the observations at various temperatures is that function of the temperature which theory requires with the exception of the lowest three temperature data given by Burnett. The conclusion is that the Burnett data indicate the presence of association.

3. The numerical equation for the fraction associated for carbon dioxide from the Joule-Thomson data, when used to compute the density coefficient for the increase in constant-volume heat capacity of carbon dioxide, gives a number $2^1/_2$ times smaller than that given by Joly based on his measurements.

4. The value of the associated fraction of carbon dioxide at one atmosphere and 220°K. as obtained from Burnett's Joule-Thomson data is 0.004. At 270°K. it is 0.00075 and at 400°K., 0.000052.

Cambridge 39, Massachusetts

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# PUBLICATIONS

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The Research Laboratory of Physical Chemistry

Serial No. 159 [illegible] 46 /1397-1403 [illegible] July, 1924

# THE MOVING-BOUNDARY METHOD OF DETERMINING TRANSFERENCE NUMBERS. II

by

Edgar R. Smith and Duncan A. MacInnes

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Vol. XLVI, No. 6. June, 1924.]

[Contribution from the Research Laboratory of Physical Chemistry,
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# THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. II

By Edgar R. Smith and Duncan A. MacInnes

Received March 18, 1924

This article describes a test of a simplification of the moving-boundary method for determining transference numbers. The method depends upon measuring, with a silver coulometer, the number of coulombs that pass through the circuit during the time it takes a single-boundary to sweep through a known volume.

The transference number $T$ obtained by the single-boundary method is given by the equation

$$T = \frac{V}{\phi}\frac{F}{Q} \qquad (1)$$

in which $V$ is the volume passed through by the boundary, $\phi$ is the volume of the solution which contains one equivalent, $F$ is 96,500 coulombs, and $Q$ is the number of coulombs passed during the measurement. The derivation of this equation is very simple. If $F$ coulombs were passed, the single boundary would sweep through a volume of $T\phi$, and for a different number of coulombs, $Q$, the volume traversed will be $V = T\phi Q/F$ which is Equation 1.

It has been shown theoretically[1] that if a boundary is to move at its theoretical velocity the concentrations of the measured and of the indicator solutions ($C$ and $C'$, respectively) must conform to the relationship,

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[1] Kohlrausch, *Ann. Physik*, **62**, 209 (1897). Masson, *Z. physik. Chem.*, **29**, 501 (1899). Denison, *ibid.*, **44**, 581 (1903). Miller, *ibid.*, **69**, 436 (1909).

$$C/C' = T/T' \tag{2}$$

in which $T$ and $T'$ are the transference numbers of the leading and following ions. Previous investigators have assumed an automatic adjustment of the indicator solution to take place which fulfills this requirement.[2] In the first paper of this series[3] the authors showed that the observed "transference number" varies markedly with the concentration of the indicator solution, except for a short range on each side of the theoretical concentration as calculated from Equation 2. The work to be described includes a further study of this variation, with a different design of apparatus, for the case of potassium chloride solutions, with lithium chloride solutions of various concentrations as indicators. In order to obtain sufficient current to give, in the coulometers, a deposit of silver which could be weighed with the required accuracy, the moving-boundary apparatus had to be made much larger than has been the usual practice. This change led to effects, described below, which convince us that the greatest usefulness of the method will not be obtained along the lines described in this research. The results, however, are interesting and will be given in some detail.

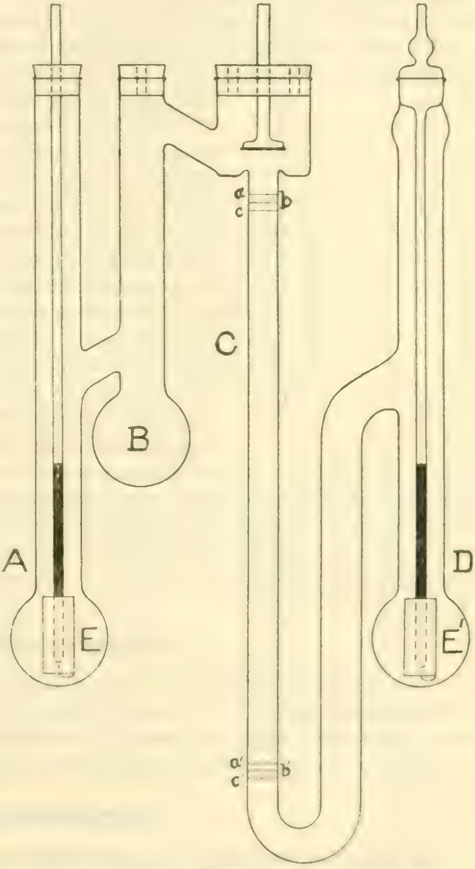

Fig. 1.

## Apparatus and Manipulation

The apparatus used differs in many details from the one described in our previous article,[3] and is shown in Fig. 1.

The electrode tubes, A and D, are far enough removed from the measuring tube C so that the concentration changes taking place in the electrode tubes during the electrolysis cannot possibly alter the concentration of the solution in C. The electrodes, E and E′, are made of platinum gauze, coated electrolytically with silver, the cathode E′ being also coated with silver chloride. Trouble was experienced due to the evolution of gas at the electrodes when these were of the form shown in Fig. 2a, the gas being mainly evolved on the wire used for sealing into the tube. This was overcome by making the electrodes in the form of a cylinder surrounding the lower end of the tube, as shown in Fig. 2b, thus reducing the current density on the upper part of the electrode where it was first attacked by the current. It was also found necessary to fill the bulb of Tube A with a more concentrated solution of lithium chloride (about 0.5 $N$) to supply the anode with sufficient chloride for the electrode reaction. Tube B acted as a trap to prevent this concentrated solution from reaching the measuring tube C. This tube had an inside diameter of 1.1 cm. as compared to one of 0.3 cm. diameter in our first apparatus. It was calibrated with mercury for three volumes between the marks a and a′, b and b′, c and c′. These marks were etched completely around the tube to eliminate errors due to parallax. The methods of filling the apparatus, forming and illuminating the boundary, etc., were the same as described in our first paper.

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[2] Denison and Steele, *Phil. Trans.*, **205A**, 449 (1906).

[3] MacInnes and Smith, This Journal, **45**, 2246 (1923).

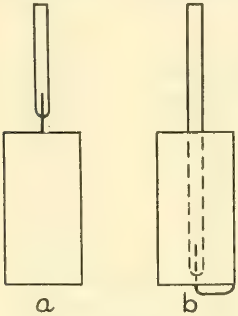

Fig. 2.

Three silver coulometers of the porous-cup type were connected in series with the apparatus in such a way that each could be independently thrown in or out of the circuit without interrupting the electrolysis. As the boundary passed each of the upper marks on the Tube C of the apparatus a coulometer was thrown into the circuit, and as it crossed each of the lower marks the corresponding coulometer was disconnected from the circuit, thus giving three independent measurements in each experiment. The general specifications for silver coulometers recommended by the Bureau of Standards[4] were followed. A current of about 35 milliamperes was used and was kept nearly constant by means of an adjustable resistance and a milliammeter in series. The weight of silver deposited was about 0.5 g. in each coulometer.

## Purification of Materials

The potassium chloride used was a C. P. product and was further purified by recrystallization and fusion. The lithium chloride was prepared from C. P. lithium carbonate and hydrochloric acid, and purified by recrystallization. The silver nitrate for the coulometers was recrystallized from slightly acid solution, and fused.

## Experimental Results

In every experiment the concentration of potassium chloride was 0.1 weight normal, that is, 7.456 g. of salt per 1000 g. of water. The density of this solution[5] at 25° is 1.0017, and therefore $\phi = 10058$ in Equation 1. Vacuum corrections have been made on the weights and the density. A series of measurements was made on this solution using, as indicators, lithium chloride solutions at a series of concentrations. All the results are given in Table I, three significant figures only being retained in the averages. A graph in which the concentrations of indicator solution are plotted as abscissas and the corresponding "transference numbers" as ordinates is shown in Fig. 3.

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[4] Rosa and Vinal, *Bur. Standards Bull.*, **13,** 479 (1916–17).

[5] Stearn, THIS JOURNAL, **44,** 670 (1922).

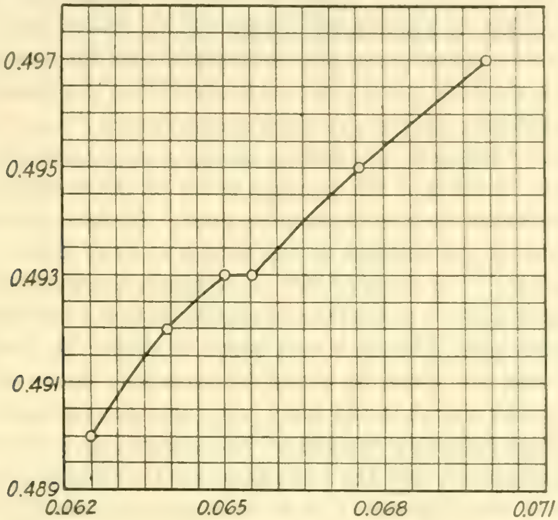

Fig. 3.

TABLE I

EFFECT OF CONCENTRATION OF INDICATOR SOLUTION ON CATION "TRANSFERENCE NUMBER" OF 0.1 $N$ POTASSIUM CHLORIDE SOLUTION AT 25°

| Concn. of LiCl | 0.06250 $T_k$ | 0.06394 $T_k$ | 0.06500 $T_k$ | 0.06548 $T_k$ | 0.06750 $T_k$ | 0.06991 $T_k$ |
|---|---|---|---|---|---|---|
| | 0.4894 | 0.4915 | 0.4925 | 0.4927 | 0.4938 | 0.4966 |
| | .4894 | .4926 | .4934 | .4928 | .4943 | .4966 |
| | .4900 | .4921 | .4928 | .4927 | .4950 | .4977 |
| | .4896 | . . | .4927 | . . | .4946 | . . . |
| | .4899 | . . . | .4925 | . . . | .4946 | . . . |
| | .4906 | . . . | .4934 | . . . | .4953 | . . . |
| Av. $T_k$ | .490 | .492 | .493 | .493 | .495 | .497 |

## Discussion

It will be seen that the observed "transference number" changes fairly rapidly with the concentration of the indicator solution, as was found in our previous communication.[3] In our earlier results, however, the curve which corresponds to Fig. 3 had a minimum at the point where Equation 2, $C/T = C'/T'$, holds, followed by a maximum on the side of more dilute indicator solutions. The minimum furnished a clear indication that adjustment to Equation 2 had been reached. In the present results, on the other hand, there is merely a break, or flat space, in the curve at and near the point where the concentrations fulfil the condition of that equation. (This point, for the solutions under consideration, corresponds to a

0.065 *N* lithium chloride solution.) With the smaller apparatus the indicator solutions had to be within about 5% of this concentration before adjustment was obtained. With this larger apparatus the indicator concentration must be apparently within 1% or less of that value before the nature of the curve gives any indication that adjustment has been reached. This would make the determination of an unknown transference number very tedious, since many more measurements would be necessary. The difference of behavior of the two pieces of apparatus was a puzzle to us until it was found that the heating effect of the current in the wider tubes is much greater than in the smaller ones. By trial it was found that the temperature of the solution in the tube was more than 1° above that of the thermostat. For some of the experiments the thermostat temperature was lowered to 23.7° so that the temperature in the tube would be about 25°. No appreciable difference was found between the results in which this was and was not done, as would be expected, since the transference numbers of potassium chloride have very low temperature coefficients.

Since the heat-radiating surface of the measuring tubes increases directly as the diameter, and the heat generated, at equal current density, as the square of the diameter, it is to be expected that this heating effect will be considerably greater in the larger tubes. Taking into account the fact that the glass walls of the tube in the smaller instrument were thinner, it is improbable that in our earlier experiments the temperature of the solution during a measurement was over 0.1° higher than the thermostat. It is this heating effect, and the unfavorable nature of the change of the "transference number" with the indicator concentration which make it appear that the larger apparatus is not the best for further work. We have not been able to suggest an explanation of the results obtained when the relation between the concentrations is not that given by Equation 2. These results when compared with our earlier ones make it appear, however, that especially when the indicator solutions are more dilute than required by that equation, the measurements are affected by the heating effect of the current.

It is of particular interest to note, however, that the transference number of potassium ion in potassium chloride, 0.493, obtained when the solutions were adjusted closely to Equation 2, agrees within the experimental error with the value, 0.492 ± 0.001, reported as a result of our previous investigation, and with the value 0.493 obtained by Denison and Steele, also by the moving-boundary method. The Hittorf and e.m.f. methods have given a somewhat higher value, 0.496, for this constant.

## Summary

A test is reported of a simplification of the moving-boundary method of determining transference numbers, which consists of measuring, with

a coulometer, the number of coulombs passed while the boundary sweeps through a measured volume. Since an enlarged apparatus was necessary, heating effects were encountered which diminish the usefulness of the method. The values for the transference numbers, however, agree with those previously obtained by this method.

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## The Effect of Hydrogen Pressure on the Electromotive Force of a Hydrogen-Calomel Cell. II. The Fugacity of Hydrogen and Hydrogen Ion at Pressures to 1000 Atmospheres

by

W. R. Hainsworth, H. J. Rowley, D. A. MacInnes

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[Contribution from the Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology, No. 160]

# THE EFFECT OF HYDROGEN PRESSURE ON THE ELECTROMOTIVE FORCE OF A HYDROGEN-CALOMEL CELL. II. THE FUGACITY OF HYDROGEN AND HYDROGEN ION AT PRESSURES TO 1000 ATMOSPHERES

By W. R. Hainsworth, H. J. Rowley and D. A. MacInnes

Received April 8, 1924

In an earlier paper[1] a description was given of a preliminary set of measurements on the electromotive force of the cell: $H_2 \mid HCl\ (0.1\ N), HgCl \mid Hg$, over a pressure range of from 1 to 400 atmospheres. The experience thus gained led us to the conclusion that if the work were to be extended to still higher pressures a number of changes in the apparatus and procedure would be advisable. These changes have been carried out and have made higher accuracy in the measurements possible. We have, further, been led to revise somewhat our conclusions as to the effect of pressure on the potential of the cell.

The chief alterations in the apparatus are: (*a*) the substitution of an absolute piston gage for the hydrostatic gages; (*b*) elimination of the bubbling of hydrogen through the solution, and (*c*) modifications of the design of the cell.

## The Cell

The cell as used in this series of measurements is shown occupying its place in the bomb, in Fig. 1.

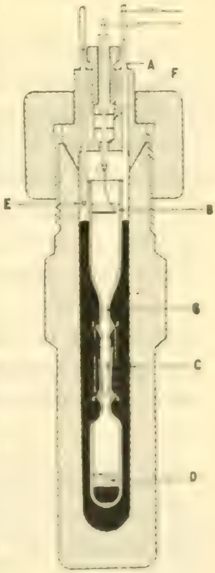

Fig. 1.

The arrangement differs from that of our previous work in that the hydrogen was not bubbled through the solution, but was simply caused to exert its pressure on the surface of the electrolyte. In order that the platinized platinum electrode could come to equilibrium with the hydrogen in a reasonable time, it was made into a disk, B, which hung in a horizontal position just under the surface of the electrolyte. The disk was, in turn, supported by a platinum wire which hooked over another wire of the same material, allowing the disk to swing freely. The agitation of the thermostat transmitted a vibratory motion to the electrode, which agitated the electrolyte. A very fine platinum wire spiral was attached to the hook and to its support to give a definite metallic connection between the two without interfering with the swinging motion of the electrode. The cell was of new design and consisted of two parts held together by a ground glass joint, C, which was held in place, as shown, by rubber bands. The lower portion held the calomel-mercury electrode, D, and was filled with electrolyte which was saturated with calomel. The upper half of the cell was filled with calomel free acid. A plug of glass wool at G prevented calomel bearing acid from reaching the platinized platinum electrode, and kept particles of platinum black out of the calomel. The glass wool was, however, omitted in some experiments without any apparent effect. The cell was supported in a metal stand, not shown in the figure. Finally, the free space in the bomb was filled with mercury. This served to connect the calomel electrode with the bomb, to which one terminal of the potentiometer was fastened, and also reduced the work of the compresser by decreasing the volume of hydrogen.

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[1] Hainsworth and MacInnes, This Journal, **44**, 1021 (1922).

Hydrogen from the compressing apparatus was led into the bomb through the tube E which was bent parallel to the surface of the mercury in order to prevent splashing of the latter due to sudden rushes of gas. The tube A served as an outlet through which hydrogen could be passed to sweep out the air in the free space in the bomb and through which, with the aid of a needle valve, the pressure could be slowly lowered.

## The Bomb

The bomb used was substantially as described in the previous communication. Some modifications were, however, made on the insulating joint F. The insulated conductor was a steel rod on which a steel ring was soldered to keep the rod from being forced out by pressure. The packing nut pressed against a hard rubber bushing under which was placed, in turn, a mica washer, a soft rubber packing, another mica washer, and a hard rubber bushing.

## The Pressure Measurements

The main improvement over our earlier work consists in the substitution of a piston gage for the dial gages. This gage consisted of a steel piston of 3mm. diameter, fitting within about 0.00005 cm. in a steel cylinder. The pressure on the piston was directly measured by placing weights on a scale pan which it supported. Since the design of a gage very similar in construction has been outlined by Smith and Taylor[2] in a recent number of THIS JOURNAL, the description will not be repeated. The calibration of the gage against a mercury column was also carried out as described by these authors. The pressures above 100 atmospheres were obtained in this work in the same way as in that already reported. The purification of the hydrogen and the measurement of the potentials of the cell were also carried out as described in the previous communication.

## The Experimental Results

The results of this series of measurements, which are given in Table I, are uniformly higher than those reported in our last series. The difference undoubtedly lies in the hydrostatic gages used in the earlier work and about which some doubt was expressed in our last paper. It now seems probable that, due to the fact that the calibration of the gages against a piston gage was not made under exactly the conditions of the experiments, the gages gave too high pressure readings. In the calibration the gages were held at each pressure for a short time only, whereas when measuring the pressure in the bomb the gages were held at the same reading for a day or more giving them time in which the moving parts could overcome any hysteresis that might be present. Our experience seems to show that the hydrostatic gages are quite unreliable for accurate work. On this account we wish the data in Table I, which were all obtained with an absolute piston gage, to supersede those in our earlier paper.

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[2] Smith and Taylor, THIS JOURNAL, **45**, 2109 (1923). See also Keyes, Smith and Joubert, *J. Math. Phys.*, Mass. Inst. Tech., **1**, 194 (1922).

TABLE I

MEASUREMENTS OF THE CELL: $H_2$ | HCl (0.1 *N*), HgCl | Hg, AT 25°, AND AT DIFFERENT PRESSURES

| Pressure Atmospheres | E.m.f. Volts | Pressure Atmospheres | E.m.f. Volts |
|---|---|---|---|
| 1.0 | 0.3990 | 701.8 | 0.4891 |
| 37.8 | .4456 | 717.8 | .4899 |
| 51.6 | .4496 | 731.8 | .4893 |
| 110.2 | .4596 | 754.4 | .4903 |
| 204.7 | .4683 | 862.2 | .4932 |
| 386.6 | .4784 | 893.9 | .4938 |
| 439.3 | .4804 | 974.5 | .4963 |
| 556.8 | .4844 | 1035.2 | .4975 |
| 568.8 | .4850 | ... | ... |

## Discussion

In our previous communication the thermodynamic equation

$$\left(\frac{dE}{dp}\right)_{C,T} = \frac{\Delta V}{F} \tag{1}$$

was derived. In this equation $E$, $p$, $F$ and $\Delta V$ are, respectively, the e.m.f. of a cell, the pressure, the faraday, and the total volume change due to the reaction occurring when one faraday passes through the cell. For the cell under consideration, in which the reaction is

$$\tfrac{1}{2}H_2 + HgCl = HCl\ (0.1\ N) + Hg \tag{2}$$

the total volume change is equal to

$$\Delta V = (\overline{V}_{HCl} + V_{Hg}) - (\tfrac{1}{2}V_{H_2} + V_{HgCl}) \tag{3}$$

Here $\overline{V}_{HCl}$ represents the partial molal volume of hydrochloric acid in a 0.1 *N* solution and the remaining terms are the molal volumes of the substances indicated by the corresponding subscripts. In order to integrate Equation 1 it is necessary to express each term of Equation 3 as a function of the pressure. The only terms which require any discussion are $V_{H_2}$ and $\overline{V}_{HCl}$. For the former, since no compressibility data are available for 25°, a series of values of the $pV$ product were computed from Keyes' equation[3] for hydrogen,

$$p = \frac{40.72\ T}{V - 9.619\ e^{(-2.898/v)}} - \frac{3.91 \times 10^{-4}}{(V - 1.18)^2}$$

in which $p$ is the pressure in atmospheres and $V$ is the volume in cc. per g. This equation agrees within the limit of error with the available data for this gas at 0°, 100° and 200° and up to 1000 atmospheres. These $pV$ products were found to be represented by the empirical equation

$$pV = RT(1 + 0.000537\ p + 3.5 \times 10^{-8}\ p^2) \tag{4}$$

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[3] Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917); THIS JOURNAL, **41**, 589 (1919).

which is slightly different from the equation for the same purpose given in our previous paper. (Because of its complex form Keyes' equation cannot be used directly for the integration.) The values of $\overline{V}_{HCl}$ can be computed from density data. However, one effect which does not seem possible of computation or independent measurement is that of dissolved hydrogen, at the higher pressures, upon this term. This will be discussed below. Aside from this effect, integration of Equation 1 yields

$$\Delta E = 0.02958 \log p + 6.12 \times 10^{-6} (p - 1) + 6.6 \times 10^{-10} (p^2 - 1) \qquad (5)$$

For the details of this integration the reader is referred to the previous paper.

In Fig. 2, the measured electromotive force of the cell is plotted in Curve A against the logarithm of the pressure. Curve B is a plot of Equation 5

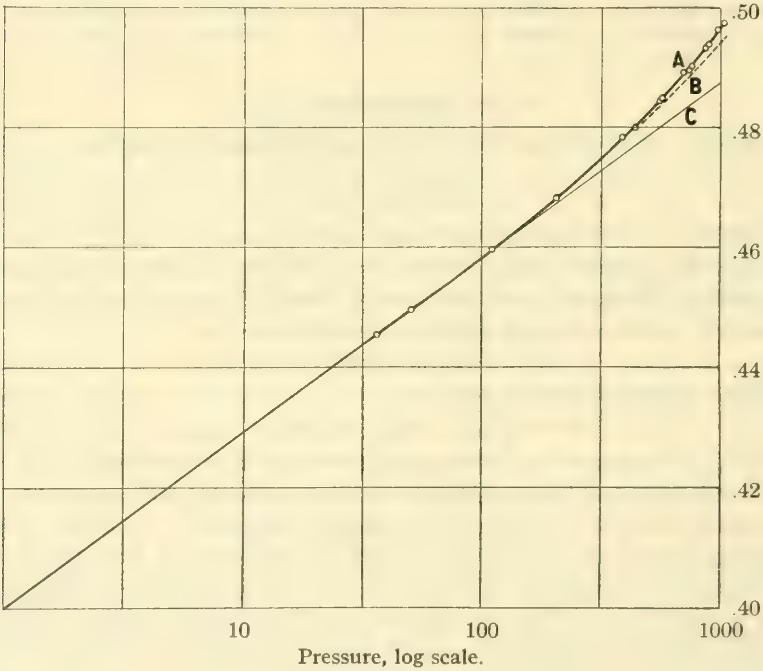

Fig. 2.

which, it will be noted, differs from the plot of the measured e.m.f.'s only at the higher pressures. The straight line, C, represents the equation $\Delta E' = 0.02958 \log p$, which would be followed if hydrogen were a perfect gas and the compressibilities of the other substances negligible or compensating.

The deviation from this "perfect gas behavior" is given as ordinates on a much larger scale against the pressures as abscissas in Fig. 3. Here, Curve A is a plot of values of $1000(\Delta E - 0.02958 \log p)$ in which $\Delta E$ is the measured increase of potential of the cell produced by the pressure $p$. Curve B is a corresponding plot of the last two terms of Equation 5. The two curves are in agreement, within the experimental error, at the lower pressures, but fall apart steadily, the deviation reaching a maximum of 2.3 mv. at 1000 atmospheres. This appears to be a real effect, almost certainly due to the increased solubility of hydrogen in the electrolyte at the higher pressures. It can be interpreted, from a thermodynamic standpoint, as has been done above, as an effect of the presence of dissolved hydrogen on the partial molal volume of hydrochloric acid. The deviation can also be looked upon as a change of hydrochloric acid as an ionizing medium produced by the presence of the gas.

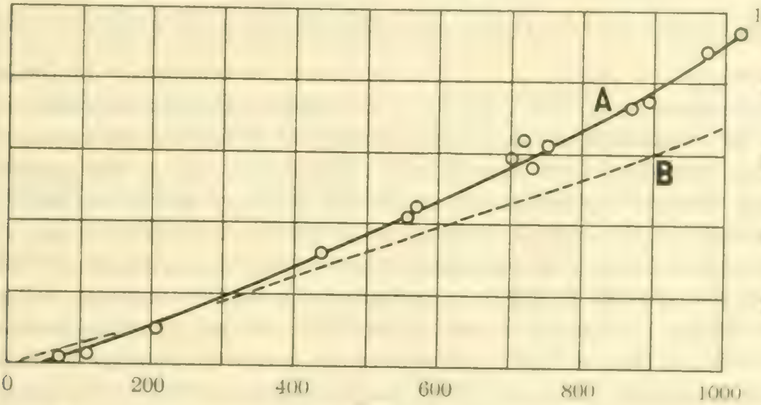

Fig. 3.

The main object of this investigation has been to study the relation of the apparent fugacity[4] of the hydrogen at a hydrogen electrode to its pressure. From a study of the electrolytic evolution of the gas it has appeared probable that at high pressures this fugacity would be higher than the pressure. This apparent fugacity may be computed from the relation, $\Delta E = \frac{RT}{2F} \log f'$, in which $\Delta E$ is the measured increase of potential of the cell produced by hydrogen pressure over the value at one atmosphere and $f'$ the corresponding fugacity, the value of the latter being taken as unity for hydrogen at one atmosphere. The apparent change of fugacity of hydrogen can be considered, with but little error, as a combination of the effects on the constituents of the reaction, $H^+ = \frac{1}{2}H_2$ since, in the first place, by far the greater part of the total change of e.m.f. with pressure is due to the properties of the hydrogen gas, and also the thermodynamic environment of the hydrogen ion is disturbed by the presence of dissolved hydrogen. The calomel electrode, on the other hand, is affected only by direct pressure, and the effect of the pressure on its e.m.f. is relatively small. As the data given in Table I and Figs. 2 and 3 show that the e.m.f. of the cell increases somewhat more rapidly than would be expected from the properties of the hydrogen gas alone, it is evident that the relative fugacity of the hydrogen ions (or the activity to which it is proportional) must decrease with pressure. As the activities of all the reacting substances increase with the pressure, this decrease of the activity of the hydrogen ion is relative to the activity *at the same total pressure.* The computed values of the apparent change of fugacity of hydrogen for a series of pressures, are given in Table II. In this table are also given (*a*) values of the actual fugacity of hydrogen, computed from the formula, $RT \log f = \int V dp$ using Equation 4 for the integration, and (*b*) values of the relative activity of hydrogen ion obtained with the aid of the equation, $\Delta' E = RT \log (1/a)$, in which $\Delta' E$ is the difference between the experimentally determined e.m.f.'s of the cell at each pressure, and that computed from Equation 5. Physically, $\Delta' E$ is the potential of a cell without transference in which the hydrogen ion in one half-cell is modified by the presence of dissolved hydrogen, and the other half-cell is assumed to be free from dissolved hydrogen, but at the same total pressure of the gas. It will be seen that at the highest pressure the apparent change of fugacity is *more than double the corresponding pressure.* This means, of course, that if the perfect gas laws were used for a computation of the effect of pressure on a hydrogen electrode at 1000 atmospheres, the error would be over 100%. Of this difference about three-fourths is due, at this pressure, to the deviation of hydrogen from the perfect gas law, and the remaining portion depends upon a relative decrease of the fugacity, or activity, of the hydrogen ions in the electrolyte. It will be seen that a comparatively small decrease of this activity, namely, 8.9%, will account for the potentials observed. This change of activity can readily be accounted for by the presence of dissolved hydrogen.

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[4] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 190.

TABLE II

FUGACITIES OF HYDROGEN AND RELATIVE ACTIVITIES OF HYDROGEN ION

| Pressure Atm. | Apparent fugacity of hydrogen Atm. | Actual fugacity of hydrogen Atm. | Relative activity of hydrogen ion |
|---|---|---|---|
| 500 | 665.0 | 656.8 | 0.996 |
| 600 | 866.6 | 832.7 | .981 |
| 700 | 1103.0 | 1027.3 | .954 |
| 800 | 1361.0 | 1243.5 | .946 |
| 900 | 1654.0 | 1479.0 | .931 |
| 1000 | 2040.0 | 1737.5 | .912 |

A rough calculation of the concentration of hydrogen dissolved in the electrolyte at 1000 atmospheres is of interest in this connection. The data of Timofejew[5] and of Geffken[6] give the solubility of hydrogen in 0.1 $N$ hydrochloric acid as 0.00158 g. per liter at 1 atm. and 25°. Multiplying this by the fugacity (1737 atm.), we obtain 2.74 g. or 1.36 moles per liter for the desired concentration. This assumes, of course, the validity of a modified form of Henry's law. It seems probable that this concentration of hydrogen is sufficient to affect the activity of hydrogen ion to the extent observed. The dissolved hydrogen reduces the mole fraction of the acid by 2.4%.

It also seems quite probable that effects similar to that just described, that is, the change of the activity of the electrolyte of a cell by the solubility of the material, or materials, reacting at an electrode, is more common than is generally supposed, and may influence the results of e.m.f. measurements under normal conditions, particularly when the electrolytes are dilute.

A factor which has been left out of the discussion is the liquid junction that must exist between the electrolyte, in which hydrogen is dissolved, and the hydrogen-free electrolyte, since the ions in the two solutions have different activities, and the two ions of the electrolyte have different mobilities. The effect of this junction is to reduce the deviations as given in Table II and Fig. 3, that is, the deviations at the electrode are larger than those stated, the cell measurements giving, of course, the net effect of the potentials present. It does not appear possible to compute this liquid-junction potential with any accuracy, but its value at 1000 atmospheres is probably of the order of a millivolt, and its sign, as has been said, is in the direction to reduce the apparent deviation.

It is hoped in the future to extend this investigation to pressures much higher than those reached during the experiments described in this communication.

## Summary

The measurements of the effect of hydrogen pressure on the e.m.f. of the cell, $H_2 \mid 0.1\ N\ HCl, HgCl \mid Hg$, as described in a previous paper, have been carried to 1000 atmospheres with improved apparatus and increased accuracy. At the highest pressure the apparent fugacity is 100% higher than the pressure. Of this difference between fugacity and pressure, about three-fourths is due to the departure of hydrogen from the perfect gas laws and one-fourth is due to a decrease in the relative activity of the hydrogen ion, due presumably to the solubility of the hydrogen.

Cambridge 39, Massachusetts

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[5] Timofejew, *Z. physik. Chem.*, **6**, 141 (1890).

[6] Geffcken, *ibid.*, **49**, 257 (1904).

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# EQUILIBRIUM PRESSURES OF INDIVIDUAL GASES IN MIXTURES AND THE MASS-ACTION LAW FOR GASES

By Louis J. Gillespie

Received July 1, 1924        Published February 5, 1925

To a surprising degree the ordinary mass-action law, based on the properties of ideal gases, suffices for the treatment of measured gas equilibria. However, the recent work of Larson and Dodge[1] on the Haber equilibrium at high pressures has shown an important deviation from the consequences of the ideal gas laws, namely, that the equilibrium constant, $K_p$, at any temperature is found to be a function of the pressure. In the absence of data to the contrary, we must now believe that $K_p$ will vary if the concentrations are varied at constant temperature and pressure —in other words, that $K_p$ is not strictly constant with respect to any change of condition whatever. Such data can therefore be used, in principle, for testing assumed forms of the mass-action law.

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[1] Larson and Dodge, This Journal, **45**, 2918 (1923); also a later paper by Larson, *ibid.*, **46**, 367 (1924).

At present we are unable to test without hypothesis even the thermodynamic consistency of data of this type. Existing pressure-volume-temperature data must be supplemented with hypotheses enabling us to pass from the properties of pure gases to those of mixtures. The fugacity rule of Lewis and Randall, which will be discussed below, contains this kind of hypothesis. The correlation of equilibrium data with equations of state is practically the mass-action problem, although the complete solution involves the untangling of implicit functions.

In practise, it is very laborious to carry out the calculations upon data secured for an equilibrium of the above type. The writer has already spent as much time as seems justifiable in view of the circumstances, without arriving at either a satisfactory thermodynamic correlation of the data or any ground for suspecting their accuracy. In the course of the study, however, certain simple considerations have become obvious which seem to merit publication because they are apparently not generally perceived. Furthermore, a simplified experimental attack on the problem has suggested itself, the theory of which presents again obvious, though perhaps novel, aspects.

Because of the various meanings of the term partial pressure, the term equilibrium pressure will be used in the following discussion to denote the pressure of a pure gas which is in equilibrium through a semi-permeable membrane with a system that contains the same gas in mixture with other gases and is at the same temperature. For greater clearness, when necessary, this pressure may be called the equilibrium pressure of the gas in the mixture. This introduces no danger of error, since two systems in equilibrium through semi-permeable membranes with the same pressure of pure gas would be in equilibrium with each other at the given temperature with respect to transfer of the given gas. The term vapor pressure has some advantages over equilibrium pressure, but is readily misunderstood.

For a thermodynamic derivation of a mass-action law a knowledge of the equations of state of the gases involved is not sufficient, even when supplemented with equations applying to the mixtures, but there is also needed some information or hypothesis concerning equilibrium pressures. In this statement, mass-action law means a relation containing concentrations determinable by analysis rather than equilibrium pressures, which would have to be determined by special equilibrium measurements. One of the few treatments of a mass-action law for real gases is that of Washburn.[2] It is worth while to emphasize that the mass-action laws under discussion in that treatment are relations containing "partial pressures" (our equilibrium pressures) rather than concentrations. The fact is not pointed out that these pressures are not calculable from any rigorous equations given.[3]

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[2] Washburn, THIS JOURNAL, 32, 467 (1910), with especial reference to pp. 484–485.

In order to fill the corresponding gap existing in the fugacity treatment, Lewis and Randall suggested the rule,[4] from a partial analogy with Raoult's law, that the fugacity of a gas in a mixture (that is, the fugacity of the pure gas at the equilibrium pressure) is equal to its mole fraction in the mixture multiplied by its fugacity when pure at the temperature and total pressure of the mixture. That is,

$$f_e = x_1 f_p \tag{1}$$

This rule reduces at large volumes to the following,

$$p_e = x_1 p^* \tag{2}$$

where $p^*$ is used, as by Lewis and Randall, to denote a very small pressure, and $p_e$ denotes the corresponding equilibrium pressure.

Now this latter relation follows directly from our kinetic ideas of very dilute gases and it supplies sufficient information about equilibrium pressures to fill the gap, if we have equations of state, not only for pure gases but also for mixtures.

Let us start with a semi-permeable membrane exposed on one side to a gaseous mixture at a very low pressure $p^*$ and of a mole fraction $x_1$ with respect to gas No. 1. On the other side is the pure gas 1 at the same temperature, and in equilibrium with the mixture through the membrane. Its pressure will then in general be denoted by $p_e$, and in this case, by our assumption, Equation 2 will hold.

Now let the pressure be increased on both sides, at constant temperature and constant composition of the mixture, in such a way as to preserve equilibrium. For maintenance of equilibrium the effect of pressure on the chemical potential, $\mu_1$, must be the same on both sides. From the Gibbs equation,

$$\left(\frac{d\mu_1}{dp}\right)_{t,n_1,n_2\ldots} = \left(\frac{dV}{dn_1}\right)_{t,p,n_2,n_3\ldots} \tag{3}$$

the right-hand member of which reduces in the case of the pure gas to $V/n_1$, it follows then that

$$\frac{V}{n_1}\,dp_e = \frac{\partial V}{\partial n_1}\,dp \tag{4}$$

or, integrating,

$$\int_{p^*x_1}^{p_e} \frac{V}{n_1}\,dp_e = \int_{p^*}^{p} \frac{\partial V}{\partial n_1}\,dp \tag{5}$$

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[3] Equations 34 and 35 on p. 484 of Ref. 2, the simple mass-action law in terms of determinable quantities, depend not merely on Boyle's and an extended Avogadro's law but also on the assumption that $p_e = px_1$.

[4] (a) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, pp. 226–227; quoted in advance of publication by (b) Bichowsky, THIS JOURNAL, **44**, 116 (1922).

In the upper limits of the integral, $p_e$ is the equilibrium pressure corresponding to the total pressure $p$ of the mixture. If we add and subtract a term before integrating we get

$$\int_{p^*x_1}^{p_e} \frac{V}{n_1} \mathrm{d}p_e = \int_{p^*}^{p} \left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p + \int_{p^*}^{p} \frac{V}{n_1} \mathrm{d}p \tag{6}$$

where the last term refers to the pure gas, but the $p$ is the total pressure of the mixture. Again adding and subtracting a term, we have

$$\int_{p^*x_1}^{p_e} \frac{V}{n_1} \mathrm{d}p_e + RT\,ln\, p^*x_1 = \int_{p^*}^{p} \left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p + \int_{p^*}^{p} \frac{V}{n_1} \mathrm{d}p + RT\,ln\, p^* + RT\,ln\, x_1 \tag{7}$$

and from the definition of fugacity it follows that

$$RT\,ln\, f_e = \int_{p^*}^{p} \left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p + RT\,ln\, f_p + RT\,ln\, x_1 \tag{8}$$

This result coincides with the rule only if the integral equals zero. But the rule cannot be restricted to a particular value of the upper limit of the integral, nor to a particular concentration; therefore, the coefficient of $\mathrm{d}p$ must be zero for the rule to hold, as otherwise the integral could not be zero for various values of the upper limit. That is, whatever the composition may be, $\frac{\partial V}{\partial n_1} = \frac{V}{n_1}$, which states that the partial molal volume of the gas in the mixture is equal to the molal volume of the pure gas at the same temperature and pressure. In other words, the correctness of the Lewis and Randall rule depends upon the exactness of an analog of Dalton's law, which states that gases do not change in volume when mixed at constant temperature and pressure.

Lewis and Randall state that their generalized Raoult's law (which includes their rule as a special case) implies among other things that the volume and heat content are additive, but they do not indicate whether the exactness of their rule demands additivity of both volume and heat content or only one of these. Having shown above that it is sufficient if the volumes are additive, we may now indicate briefly a proof that if the volumes are additive the reversible heat of mixing will also be zero, so that the heat content will be additive and *vice versa*.

Consider again the system with a semi-permeable membrane discussed above. The system is analogous to a system discussed by Planck[5] consisting of vapor and salt solution and his Equation 176 can be applied to our case. This equation gives on multiplying both sides by $\Delta V$

$$\Delta V \left(\frac{\mathrm{d}p_e}{\mathrm{d}T}\right)_c = \frac{\lambda_c}{T} \tag{9}$$

Now $\left(\frac{\mathrm{d}p_e}{\mathrm{d}T}\right)_c$ is finite, so that if either $\Delta V$ or $\lambda_c$ is zero, the other must

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[5] Planck, "Treatise on Thermodynamics," translated by Ogg, Longmans, Green and Co., **1903**, p. 197. It is also given, for instance, in MacDougall's "Thermodynamics and Chemistry," John Wiley and Sons, Inc., New York, **1921**, p. 168.

**Equilibrium Pressures of Individual Gases in Mixtures and the Mass-action Law for Gases,** by Louis J. Gillespie.

P. 308. The author writes as follows.

In the paragraph beginning at the bottom of p. 308, there is a brief discussion, involving Equation 9, based on an argument by analogy. The sentence immediately preceding this paragraph and the sentence immediately following it are concerned with this argument. This analogy is imperfect and the above portions of the text should be disregarded, since they do not really lead to that part of Conclusion 3 in the summary which deals with heat content. In the interest of accuracy, Conclusion 3 should therefore read, "It is then shown that if either of the two propositions, exactness of the rule and additivity of volumes, holds at a particular temperature, the other also will hold at the same temperature."

also be zero. The quantity $\lambda_c$ is the heat absorbed when a small unit of mass is reversibly transferred from pure gas to a large quantity of mixture of composition $c$ and can readily be shown to equal the difference of the partial heat contents per unit of mass.[6] $\Delta V$ is the corresponding volume increase.

Of the three propositions—exactness of the Lewis and Randall rule, additivity of volumes, additivity of heat content—proof of any one is sufficient to prove the other two, providing we assume Equation 2 when necessary.

It is known that the rule of additive volumes is not generally exact. To be sure, the large deviations reported by Fuchs[7] were calculated, and not directly observed and are possibly all wrong; at any rate, the writer has confirmed Dalton's law within the experimental error (about 0.2%) in the case of a mixture of oxygen and atmospheric nitrogen at room temperature and one atmosphere. On the other hand, Masson and Dolley[8] have found in careful experiments on binary mixtures of oxygen, argon, and ethylene that the law of additive partial volumes fails worse than Dalton's law itself.

The integral $\left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p$ can be evaluated graphically from an assumed equation of state for mixtures, the lower limit being taken as zero, since the area from zero to the pressure $p^*$ is as small as we please to consider it. Van der Waals assumed that the equation of state for a mixture has the same form as for a pure gas, and that the constant $b_m$ for the mixture may be approximately calculated by the rule

$$b_m = b_1x_1 + b_2x_2 + \ldots\ldots \tag{10}$$

Professor Keyes[9] has reason to believe, from unpublished calculations on the M. I. D. tables[10] for mixing nitrogen and hydrogen and from recent unpublished observations, that this rule may be correct when applied to all the constants[11] of the Keyes equation.

It is to be emphasized that a determination of the mixture equation will bring with it a complete solution of the mass-action law for compressed gases, unless we should be forced to give up the attractive assumption given above in Equation 2. Naturally, such a solution will be too complex mathematically to be of convenient use in the calculation of concentrations, since these enter in a highly implicit manner.

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[6] Compare Ref. 4 a, pp. 89–90.

[7] Fuchs, *Z. physik. Chem.*, **92,** 641 (1917).

[8] Masson and Dolley, *Proc. Roy. Soc.*, **103A,** 524 (1923).

[9] F. G. Keyes, private communication.

[10] Munitions Inventions Dept., Ministry of Munitions, Nitrogen Products Committee, *Physical and Chemical Data of Nitrogen Compounds.* From the M. I. D. Research Laboratory, University College, London, **1918.**

[11] Including, of course, the square root of $A$ in $A/(v + b)^2$ which root, as well as all the other constants, is expressed per mole or unit mass.

Using this mode of compounding the constants in the Keyes equation, the writer tried to check the Larson and Dodge data at 400°, after smoothing for temperature, but found that the use of the integrals $\left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) \mathrm{d}p$ did not lead to an improved agreement. So much uncertainty attaches to the values of the constants in the equations for the pure gases, especially ammonia, that no conclusion could be drawn, save that it is unprofitable to apply so complicated a calculation to so complicated an equilibrium in the present state of our knowledge of the constants of the gases. Other hypotheses as to equilibrium pressure were tried—subject to the same uncertainties. One of these hypotheses was that

$$p_e = \int_o^{n_1} \left(\frac{\mathrm{d}p}{\mathrm{d}n_1}\right)_{t,v,n_2,n_3} \mathrm{d}n_1 \qquad (11)$$

where the right-hand side is the analog of the Gibbs partial volume and may well be designated partial pressure. In the integration the composition, temperature and volume are held constant, the number of molecules of all kinds being increased from zero until there are $n_1$ molecules of gas No. 1, for which gas $p_e$ represents the equilibrium pressure. Applied to perfect gases it coincides with the ordinary ideal-gas partial pressure. It may be integrated in terms of known functions when applied to the van der Waals equation with the above mode of compounding constants. The results differed from the results of the first-mentioned calculations, even when the integration of Equation 11 was carried out graphically using the Keyes equation.

The method of testing the consistency of equilibrium data and equations of state consists in principle in calculating the change of the $t$-$p$-thermodynamic potential $U - TS + PV$ for the change of state—pure reactants at arbitrary pressure giving pure resultants at the same pressure and temperature. This change must be independent of the pressure and concentrations in the equilibrium box, which pressure and concentrations are given by the equilibrium data used. This is of course equivalent to calculating fugacities and substituting in the simple mass-action expression, to see whether this is constant. There is naturally no special virtue in fugacity, although it is mathematically very convenient in certain special calculations when $V\mathrm{d}p$ cannot be integrated in terms of known functions from the equation of state used.

Even when checks are obtained in such a calculation, they may be due to compensations, the individual equilibrium pressures or fugacities possibly being greatly in error. In the course of much unreported calculation I have observed such large compensation at work. For a good control a simpler equilibrium must be chosen, so that individual equilibrium pressures can be measured and calculated.

The ideally simple equilibrium system would be hydrogen separated by a palladium membrane from a mixture of hydrogen and inert gas. Since palladium is not rapidly permeated at low temperatures and hydrogen is a relatively perfect gas, especially at high temperatures, this system is not so very promising and apparently has not been carefully studied from this point of view, though Löwenstein[12] has introduced such a membrane into the study of equilibria, assuming ideal-gas relationships. The following method is in principle nearly as simple and is more general in certain respects.

We may use as the equivalent of a semi-permeable membrane a system of mutually insoluble solid phases ($n$ in number) which together with a pure gas phase form a univariant system. At a definite temperature these solid phases will have a definite equilibrium pressure, determinable by experiment. Then an inert gas may be introduced and the equilibrium concentration in the gas phase and total pressure may be measured. From the densities (or eventually also the compressibilities) of the solid phases, we may calculate the equilibrium pressure of the solid phases under the increased external pressure. This result must then be equal to the equilibrium pressure of the active gas in the mixture of known temperature, pressure and composition and can be regarded as the experimentally determined equilibrium pressure of the gas in the mixture.

It is a reasonable expectation that the solid phases will not dissolve enough inert gas to require a correction. Such a solubility would mean that the substitute for a semi-permeable membrane is imperfect. The advantage of choosing a univariant system is that the addition of inert gas will in general change the masses of the solid phases, but in the case of a system which is univariant the equilibrium pressure of the solid phases will be unaffected and therefore no analysis of the solids will be necessary. It is necessary only to ensure that none has entirely disappeared. This may be done by addition of active gas, when the total pressure must be unchanged after re-establishment of equilibrium.

A limitation is imposed on the variety of data which can be obtained in this way from the given solid phases, due to the fact that the total pressure is a function of the composition.

One way of justifying the foregoing theory is by reference to the Gibbs theory. Gibbs always divided the energy, entropy, etc., of a system among the individual phases, in consequence of which any component possessed a potential, a partial volume, etc., in each phase. There is no logical necessity for always doing this. We may better, in a special treatment of univariant systems, divide the energy, entropy, volume, etc., as follows: one portion to the gas phase, the rest to the condensed phases taken collectively. We shall refer to the solid phases, assumed to be mutually insoluble, as the condensate. The condensate has then a potential, a partial molal volume, etc., with respect to a given component and the Gibbs theory applies to these quantities just as to the usual quantities distributed among individual phases, the arguments not being changed. In particular, the change of potential with (total) pressure is measured by the partial volume per unit of mass, but now the partial molal volume of the condensate, unlike that quantity for a pure substance, is physically interpretable, being in fact the algebraic sum of the molal volumes of the solids entering into the reaction in question. Therefore the change of equilibrium pressure of the condensate with external pressure can be calculated from the partial molal volume, as was assumed in the foregoing theory. Since the equilibrium pressure of a condensate is not dependent upon the mass ratios of its constituents, the value of its potential must also be independent.

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[12] Löwenstein, *Z. physik. Chem.*, **54**, 715 (1906). In Ramsay's experiments [*Phil. Mag.*, [5] **38**, 206 (1894)] equilibrium was obviously not attained, nor especially sought.

Experimentation is at present in progress on the determination of the equilibrium pressure of ammonia in mixture with nitrogen, using some of the compounds of metal halides with ammonia as a virtual semi-permeable membrane, in the hope of being able to correlate the results with pressure-volume-temperature data on the gases.

## Summary

1. The mass-action law for real gases is briefly discussed. No proposed exact equations permit calculation of equilibrium concentrations from equations of state of pure gases. The upper limits in the integrals of $Vdp$ are still unknown, being called here "equilibrium pressures" (of single gases in mixtures).

2. The rule of Lewis and Randall for calculating the fugacity of a gas in a mixture would suffice, if it were exact. An exact rule is given with an added term containing the integral from zero to the total pressure of $\left(\frac{\partial V}{\partial n_1} - \frac{V}{n_1}\right) dp$, based on the assumption that at great volumes the equilibrium pressure is equal to the ideal-gas partial pressure.

3. With the aid of this assumption, when necessary, it is shown thermodynamically that all three propositions—exactness of the rule, additivity of volumes and additivity of heat content—follow from any one of the three.

4. Equilibria involving three gaseous species are too complicated to permit a critical test of such rules, owing to compensation of errors. To provide an attack on the simplest case a method of experimentation is outlined for determining equilibrium pressure by means of a virtually semi-permeable membrane, consisting of the solids of a univariant system. The thermodynamic discussion involves attributing chemical potentials and partial volumes to the condensed mass of solid phases, which are considered collectively as if they were a single phase in the Gibbs treatment.

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# The Representation of the Haber Equilibrium Data by an Equation

by

Louis J. Gillespie

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(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 163.)

# THE REPRESENTATION OF THE HABER EQUILIBRIUM DATA BY AN EQUATION[1]

By Louis J. Gillespie

**1. Introduction.** Not long ago two papers were published from the Fixed Nitrogen Research Laboratory, United States Department of Agriculture, on the Haber equilibrium, the equilibrium between nitrogen, hydrogen, and ammonia. The first paper was published by Larson and Dodge[2], and dealt with pressures from 10 to 100 atmospheres; the second, by Larson[3], dealt with pressures from 300 to 1,000 atmospheres. These data prove definitely that the equilibrium constant in terms of "partial pressures," $K_p$, which for ideal gases is a function only of the temperature, is in this case a (smaller) function of the pressure also.

Over a year ago the writer made an unsuccessful attempt to correlate these data thermodynamically with the aid of various hypotheses relating to mixtures of gases[4]. For this purpose the data were first smoothed for temperature. As a preliminary to another such attempt the writer has recently carried out a smoothing of the data for both temperature ($T$) and pressure ($p$) by a non-thermodynamic method, and the quite unexpected results of this purely empirical smoothing are here reported. Table I gives the values of $K_p$ used for the present calculations.

The problem is to pass a surface near the points plotted in space using suitable functions of $K_p$, $T$, and $p$ as coördinates. The form of the surface and the values of the coefficients must be

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[1] A brief summary of the results of this paper appeared in the Proceedings of the National Academy of Sciences, **11**, 73 (1925).

[2] Jour. Am. Chem. Soc., **45**, 2918 (1923).

[3] Jour. Am. Chem. Soc., **46**, 367 (1924).

[4] Dr. Larson very kindly gave us these data in advance of publication. The present smoothing was however begun eight months after the second paper of Dr. Larson was published.

TABLE I. Observed Equilibrium Constants of Fixed Nitrogen Research Laboratory

| Temperature, °C. | *Pressure in Atmospheres* 10 | 30 | 50 | 100 | 300 | 600 | 1,000 |
|---|---|---|---|---|---|---|---|
| 325 | 0.0401 | ...... | ...... | ...... | .... | .... | .... |
| 350 | .0266 | 0.0273 | 0.0278 | ...... | .... | .... | .... |
| 375 | .0181 | .0184 | .0186 | 0.0202 | .... | .... | .... |
| 400 | .0129 | .0129 | .0130 | .0137 | .... | .... | .... |
| 425 | .00919 | .00919 | .00932 | .00987 | .... | .... | .... |
| 450 | .00659 | .00676 | .00690 | .00725 | 0.00884 | 0.01294 | 0.02328 |
| 475 | .00516 | .00515 | .00513 | .00532 | .00674 | .00895 | .01493 |
| 500 | .00381 | .00386 | .00388 | .00402 | .00498 | .00651 | .... |

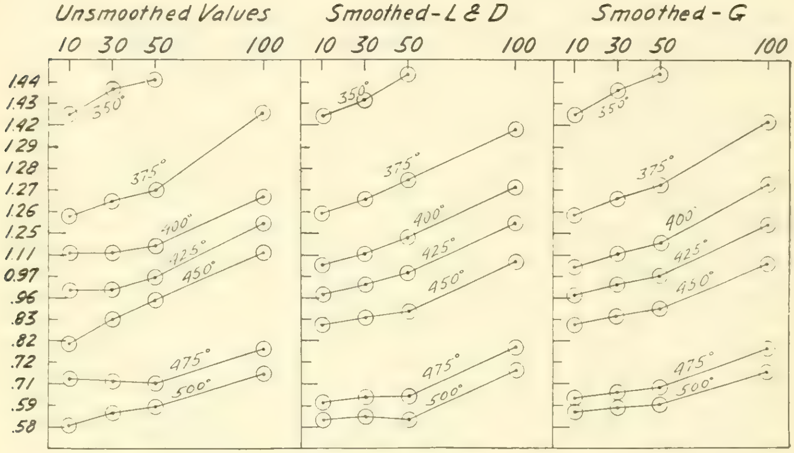
found at the same time. This requires that the element of judgment be added, and the success attained depends inversely on the arbitrariness of the judgments introduced. When there is only one independent variable, experience has shown that inflexions are presumptively to be avoided, and not to be represented unless the data strongly indicate them. In the same way we must avoid wrinkles or sudden changes of curvature when passing a surface near experimental points, unless the data strongly confirm them. Given this presumption, the problem may become practically definite in special cases in which various critics will agree that little arbitrariness of judgment is required. In such a case interpolated values given by the surface should be nearer the unknown true values than were the original unsmoothed data.

There is a natural inclination to judge the success of the smoothing by the size of the residual differences, between observed and calculated values. This inclination is stronger when we forget that precision of data is often better than the definition of the subject material or of the experimental circumstances. As a matter of fact, smoothing for several variables is a valuable method of determining in a given case whether precision exceeds definition or not.

2. **Treatment of the Low Pressure Data of Larson and Dodge.** In order to decide, with respect to which variable first to smooth, since the forms of the functions were not known, the original

values of log $K_p$ (after addition of 3 to avoid minus signs) were plotted as a function of the pressure, from 10 to 100 atmospheres at constant temperature, with the result shown in the left-hand drawing of Fig. 1. Any decision upon a suitable smoothing function for these isotherms would seem arbitrary. When, however, the original values of log $K_p$ were plotted as a function of $1/T$ at constant pressure, the data were found to be very consistent, the isobars all obviously being straight, or so nearly so that no curvature could be established. The slopes of these isobars show no detectable sudden changes from 10 to 100 atmospheres. The plot is given in Fig. 2. The differences between the observed values and those calculated from the best straight lines will be included in Table III and the case can critically be judged by inspection of these differences as to magnitude and sign.

Fig 1: Values of Log Kp +3 as Function of the Pressure (10-100 Atm).



The sudden jumps in the values of the ordinates are due to displacing the zero of the scale for each isotherm. The isotherms are, however, plotted to the same scale. The same applies to Fig. 2.

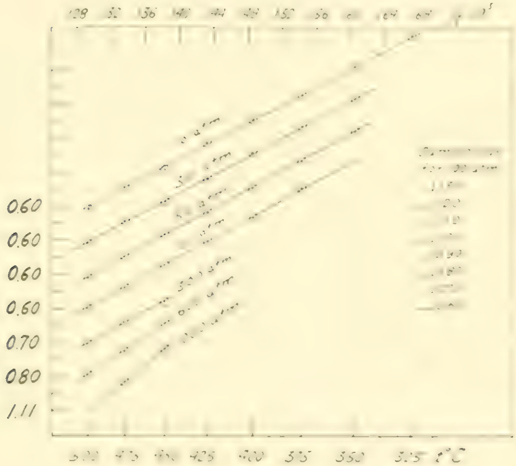
From an empirical standpoint there is a minimum of arbitrariness, therefore, in writing for the smoothing function at constant pressure:

$$\log K_p = s\ 1/T - b \qquad (1)$$

The values of $s$ and $b$ were determined for each pressure by the method of least squares and without weighting, to minimize personal bias, and the probable errors of $s$ and $b$

$$(0.67\sqrt{(vv)/(m-2)p_x})$$

Fig. 2. Unsmoothed Values of Log $K_p + 3$ as Function of the Reciprocal Temperature

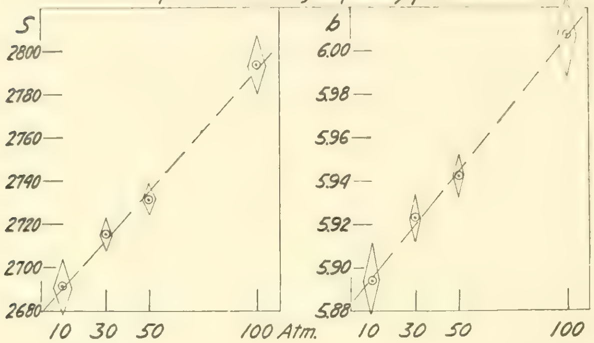


were also determined. In all the calculations $T = t + 273.1$, and common logarithms are used.

The values of log $K_p$ calculated from these values of $s$ and $b$ are plotted in the right-hand drawing of Fig. 1. The curves in the middle drawing give the corresponding values calculated from the smoothing equations given by Larson and Dodge. It is evident that smoothing for temperature by either their five-constant equations or the equations (1) improves the appearance of the pressure variations.

These values of $s$ and $b$ in equations (1) were then plotted as functions of the pressure, with the result shown in Fig. 3. The vertical diameters of the diamonds are equal to the probable errors The broken straight lines are those calculated by the method of least squares, weighting the points with weights equal to the reciprocals of the probable errors. The effect of the weighting is very slight. The points, of course, cannot lie exactly on the lines, as the data have not previously been smoothed for pressure.

Fig. 3: Pressure Variation of Constants $S$, $b$ in Equations $\log K_p = s\,1/T - b$



There appears to be but little of the arbitrary[5] in writing for the parameters

$$s = Bp + A \tag{2}$$

and

$$b = Dp + C. \tag{3}$$

Combining these results we get

$$\log K_p = (A + Bp)1/T - (C + Dp) \tag{4}$$

which for this low pressure work becomes

$$\log\ K_p = (2679.35 + 1.1184\ p)\ 1/T - (5.8833 + 0.001232\ p) \tag{5}$$

3. **Treatment of the Whole Body of Data together with Haber's Best Data.** Similar calculations were made, using the high pressure data of Larson. The case for the straightness of the isobars, though not so strong, is good. There are fewer points, in no case

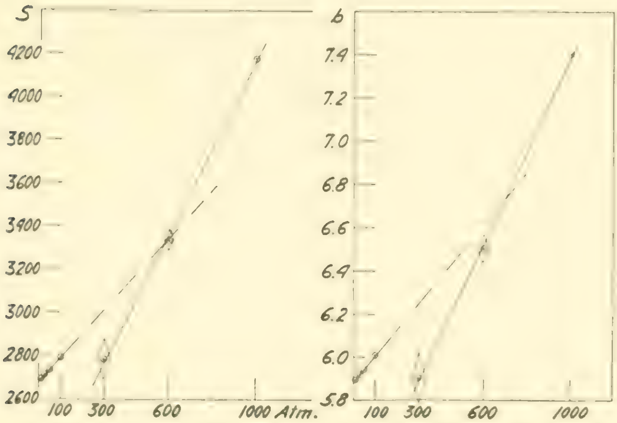
---

[5] With regard to the discrepancy next to be pointed out the reader will observe that this discrepancy will only be increased if we pass, instead of straight lines in Fig. 3, the alternative curves with inflexion.

more than three on the isobar, and there is no consistent curvature, as may be seen later by inspection of Table III.

When the slopes and intercepts of the best isobars are plotted as functions of the pressure, together with those for the low pressure data on the same scale, the striking picture shown in Fig. 4 results. The data are discontinuous, the point of discontinuity lying between the two sets of data. The diamonds show again the probable errors, which have naturally for the high pressures but slight value. The probable errors for the low pressure data are so small as to lie within the circles. It is not possible in either case to draw a curve without a physical discontinuity near the points within the probable errors. If the lines do not remain well within the probable errors it is found in this case that the data will be badly represented by the lines. It would be an arguable question whether this consideration ought not to be entirely neglected and (very arbitrary) lines without inflexion drawn near all the points, but for the facts to be discussed in the next three paragraphs.

*Fig. 4: Pressure Variation of Constants S, b in the Two-Constant Equations*



In the low pressure work many more points were measured than in the high pressure work, and equilibrium was approached from both sides, thus at least doubling the weight to be given to the low pressure points. Thus the discrepancy cannot cast doubt on the low pressure data, and it is unnecessary to cast doubt on the precision of the high pressure data. There is little or no question as to the exact composition of the original gas delivered to the catalyzer in the low pressure work. In the high pressure work, however, the exact composition is not stated. It is, however, necessary to have a value in order to calculate $K_p$ from the equilibrium percentage of ammonia. Through the courtesy of Doctors Larson and Dodge I learn that this composition was taken in this calculation to be the same as in the low pressure work. They pointed out in their paper that "a 10% variation in the 3:1 hydrogen-nitrogen ratio produces an error of only 0.2% in the equilibrium constant." I wish to point out that such a statement can apply only to the above calculation, and not to any questions of fact, and the statement does not contradict my opinion that a 10% variation in the 3:1 ratio will in fact produce an experimental variation of much more than 0.2% in the equilibrium constant. This is supported by comparison of Haber's data for 30.09 atmospheres with the later work of Larson and Dodge. For the comparison, some extrapolation is necessary. Least squaring of Haber's best data[6] for 30.09 atmospheres gives the values for $s$ and $b$, 2880.36 and 6.1264, which may be compared with the values in equation (5). A difference of 0.09 atmosphere makes only a microscopic difference in the constants $s$ and $b$, and does not here affect the fourth decimal place in log $K_p$. The fairness of the form of equation (1) as applied to Haber's results may be judged by the deviations: 1,000 times calculated minus observed log $K_p$; given in Table II.

TABLE II. Representation of Haber's 30 atmosphere data by the equation: log $K_p = 2880.36\ 1/T - 6.1264$.

| Temperature, °C. | 561 | 620 | 631 | 704 | 710 |
|---|---|---|---|---|---|
| $10^3$ (calc.-obs.) log $K_p$ | −0.7 | −2.0 | +2.6 | +4.3 | −6.9 |

| Temperature, °C. | 722 | 812 | 914 | 952 |
|---|---|---|---|---|
| $10^3$ (calc.-obs.) log $K_p$ | +3.0 | −0.3 | +1.1 | −1.4 |

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[6] Haber. Ztschr. f. Elektrochem., **20,** 597 (1914). The H. and L. figures were not used.

The greatest deviation, 6.9, amounts to 1.6% error in $K_p$ itself, and it is obvious that these data are of practically the same degree of consistency as those of Larson and Dodge at similar pressures (see Table III). It appears justified to extrapolate Haber's values by means of this equation to 500° C., which gives $\log K_p + 3 = 0.5993$. Comparing this with the values 0.5866, 0.5887, and 0.5888, which are in turn (1) the L. and D. measured value, (2) my temperature-smoothed value from L. and D., and (3) the $T$ and $p$ smoothed value from equation (5); there is seen to be a difference in the logarithms of 0.0127 or 0.0106. The latter difference corresponds to a difference of 2.5% of $K_p$ itself, which is outside the apparent experimental error of either set of data. To examine whether this asserted difference is dependent upon the form of function used for the temperature smoothing we may compare the percentage of ammonia calculated by Larson and Dodge for 500° and 30 atmospheres with the value calculated by Haber. These values are given by Larson and Dodge as 3.49 and 3.62% ammonia, respectively. In the calculation of these values, a Nernst heat-theorem equation was used in each case. These values lead to values of $K_p$ which differ by 4%, Haber's value again being the greater, so that the thermodynamic smoothing does not fail to reveal the discrepancy.

It is hardly permissible to attribute this difference to experimental error, in view of the great care and labor expended by both German and American investigators.[7] It is justifiable to accept the findings as facts, and to conclude that the 2.5% variation in $K_p$ is due to the known 6% variation in the 3:1 hydrogen-nitrogen ratio. This ratio was 3.24 in the Larson and Dodge work and 3.06 in Haber's work. The concomitant small variation in the small argon-hydrogen ratio is presumably of little importance.

In view of the very good consistency which the high pressure data of Larson exhibit when taken alone, a separate equation (6) was therefore derived for the high pressure data.

$$\log K_p = (2172.26 + 1.99082\ p)\ 1/T - (5.2405 + 0.0021550\ p) \quad (6)$$

---

[7] The experiments of Greenwood (Ztschr. f. Elektrochem. **21**, 241 (1915) do not have to be considered as a part of Haber's equilibrium data, as they were not planned to furnish $K_p$ values, but to determine the practical efficiency of a catalyzer. Greenwood did not even calculate $K_p$ values.

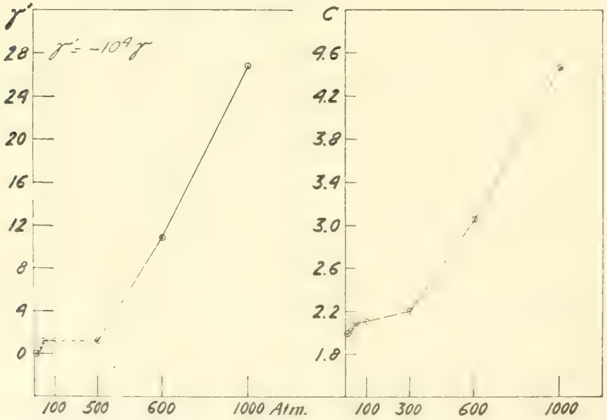
When equations (5) and (6) are both extrapolated to 200 atmospheres and the calculated $K_p$ values are compared, the discrepancy in $K_p$ is only 5.6% at 450° and −1.7% at 500°. Such differences might reasonably be accounted for by an assumed variation of 10% in the hydrogen-nitrogen ratio.

In a recent article[8] it has been pointed out that in a case like the present one, where $K_p$ varies with pressure, it must also vary with the composition, and we should expect only a small effect corresponding to the small variation with the pressure. Such statements cannot be proved by thermodynamics alone, because no rigorous equations containing $K_p$ exist, the function $K_p$ having been introduced by means of the ideal gas laws. Such statements, once made, will, however, be regarded as obvious.

It should be emphasized that the discrepancy is a second order effect, since intentional variations of composition were not made, and it cannot be perceived until an attempt is made to smooth simultaneously for temperature and pressure.

The discrepancy is also revealed when the five-constant equation from the Nernst heat-theorem is used for the temperature smoothing, as is shown by Fig. 5.[9] This shows as functions of the

Fig. 5: Pressure Variation of Constants $\gamma'$, $C$ in the Five-Constant Equations



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[8] Gillespie, Jour. Am. Chem. Soc., **47**, 305 (1925).

[9] The second abscissa should be 300 instead of 500.

pressure the two constants calculated by Larson and Dodge and by Larson. The other three constants are not varied with the pressure. In the writer's opinion, straight lines cannot be passed sufficiently near the low pressure data, disregarding the high pressure data, to represent the data within the experimental error. Therefore we are at a loss to know how to proceed, when we smooth for temperature in this way. In general, smoothing by the empirical two-constant equation appears better than by the five-constant equation, but the superiority does not appear until we begin to smooth for both variables. Haber noted a similar fact in discussing the pressure variation from 1 to 30 atmospheres[10], and noted that a smaller value of $Q$ (our $s$) must be used at 1 atmosphere. He seems to have considered this latter fact as an objection, considering the two-constant equation as a mere approximation of the more theoretical five-constant equation. A theoretical advantage may, however, be illusory in a case where the ideal gas laws are now definitely known to be failing.

It is in fact noteworthy that the five-constant equation is no worse in this case, because similar equations have many times been applied to simpler, univariant, equilibria, and almost invariably the believers in the equation have been forced to conclude that the data are erroneous. This was without necessity of smoothing for a second variable. In one of these cases Keyes and Hara[11] recently proved the older data correct, and the equation wrong.

The Gibbs phase rule leads to the expectation that $K_p$, like any other internal variable of the system, be in this case a function of four variables; for instance, the temperature, pressure, and the ratios $H:N$ and $Ar:N$[12]. These ratios may refer, for convenience in industrial application, to the original gas mixture delivered to the catalyst, providing arbitrary changes are not subsequently made. In the present case the ratio $Ar:N$ was practically constant, but it has not been so in all the earlier experimentation.

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[10] Ztschr. f. Elektrochem., **21**, 89 (1915). Especially p. 105.

[11] Jour. Am. Chem. Soc., **44**, 479 (1922).

[12] When the gases are ideal, the ratios disappear as variables, since they are incorporated into the function $K_p$ in just the proper manner.

4. **Representation of the Data by the Equation.** It remains to compare the original unsmoothed data (*A*), with values calculated from the individual equations (1); (*B*), with values calculated from the individual equations given by Larson and Dodge and by Larson; and (*C*), with values calculated from equation (5) up to 100 atmospheres and from equation (6) from 300 to 1,000 atmospheres. In Table III are plotted, after multiplication by 1,000, the differences: calculated log $K_p$ minus observed log $K_p$ for all the data. The two mean differences, with, and without respect to sign, are also given[13]. Inspection of this table shows that the two-constant equations represent the data as well as, or slightly better than, the five-constant equations. The three constants which are not functions of the pressure possibly interfere somewhat with the success, from an empirical standpoint, as the means with respect to sign show a small consistent deviation. The remarkable consistency of the low pressure data, 10–100 atmospheres, is demonstrated by the fact that the surface (5) passes practically as near the points (disregarding the sign of

TABLE III. *The differences, calculated minus observed log Kp, from*

*A, 1/T smoothing; B, L. & D. smoothing; C, 1/T and p smoothing.*

| | 10 | | | 30 | | | 50 | | | 100 | | | 300 | | | 600 | | | 1000 Atm. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $t°$ | A | B | C | A | B | C | A | B | C | A | B | C | A | B | C | A | B | C | A | B | C |
| **325** | +2.5 | -08 | -0.1 | | | | | | | | | | | | | | | | | | |
| **350** | +0.2 | -0.5 | -6.5 | -1.9 | -5.0 | -2.6 | -2.6 | -0.9 | +0.9 | | | | | | | | | | | | |
| **375** | +0.8 | +1.5 | -1.8 | +13 | +0.4 | +09 | +2.8 | +53 | +6.1 | -2.7 | -7.6 | -5.1 | | | | | | | | | |
| **400** | -6.4 | -5.1 | -8.9 | 0.0 | 00 | -0.3 | +19 | +4.0 | +5.0 | +59 | +5.2 | +3.7 | | | | | | | | | |
| **425** | -2.3 | -1.4 | -47 | +2.8 | +29 | +26 | +1.1 | +1.9 | +4.0 | -0.3 | 0.0 | -14 | | | | | | | | | |
| **450** | +87 | +8.8 | +62 | +1.5 | +1.1 | +1.5 | -3.8 | -5.1 | -1.2 | -49 | -35 | -69 | +3.6 | +3.3 | -35 | -19 | -3.3 | +10.5 | 0 | +0.3 | -5.4 |
| **475** | -9.4 | -10.9 | -11.8 | -5.8 | -7.5 | -5.8 | -1.3 | -5.3 | +1.2 | +0.5 | +1.9 | -1.4 | -7.3 | -7.9 | -13.7 | +4.0 | +3.8 | +15.0 | 0 | +03 | -48 |
| **500** | +6.0 | +2.6 | +3.5 | +21 | -1.3 | +2.2 | +20 | -54 | +4.4 | +1.5 | +2.2 | -0.3 | +3.8 | +2.3 | -1.8 | -2.0 | -3.3 | +7.8 | (No data) | | |
| Mean | 0 | -0.7 | -3.0 | 0 | -13 | -0.2 | 0 | -0.8 | -29 | 0 | -03 | -16 | 0 | -0.8 | -63 | 0 | -0.9 | +11.1 | 0 | +0.3 | -51 |
| Mean | 45 | 40 | 5.4 | 22 | 26 | 2.0 | 2.2 | 4.0 | 33 | 2.6 | 34 | 3.1 | 49 | 45 | 63 | 2.6 | 3.5 | 11.1 | 0 | 0.3 | 5.1 |

*Values are multiplied by 1000.*

5. corresponds to 12% in Kp
10 " " 23 - - -
15. " " 35 - - -

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[13] The first mean under 50 atmospheres, *C*, should be +2.9. Several decimal points have been lost in the cut, but they are obvious.

the deviations) as do the individual lines determined without pressure smoothing. The representation of the data from 300 to 1,000 atmospheres by the surface (6) is reasonably good, aside from the consideration that the ratio $H:N$ may have changed between points to a certain extent[14].

## Summary

1. The equation:

$$\log K_p = (2679.35 + 1.1184\ p)\ 1/T - (5.8833 + 0.001232\ p)$$

represents within the experimental error the equilibrium constant values determined by the Fixed Nitrogen Research Laboratory over the temperature range about 325° to 500°C and from 100 atmospheres to the lowest pressures. The equation is serviceable for calculating "$K_p$" exactly for an equilibrium mixture resulting from the use of a reacting mixture made from atmospheric nitrogen and having a hydrogen-nitrogen ratio equal to 3.24.

2. The equation:

$$\log K_p = (2172.26 + 1.99082\ p)\ 1/T - (5.2405 + 0.0021550\ p)$$

represents well the high pressure data of the same laboratory, but not so many decimal places are serviceable in this case, because the hydrogen-nitrogen ratio is less definitely known.

3. An attempt to construct one equation for both high and low pressure data fails because of a discontinuity, which is too small to be shown by plotting of isobars, but is strikingly exhibited when the pressure variations of the parameters of the isobars are

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[14] If values of the equilibrium percentage of ammonia are desired, the calculation can be made for the low pressure data, and must be made for the high pressure data, by means of the approximate equation: $K_p = 3.083\,a / [(0.997 - a)^2 p]$, since this was used in the calculation of the $K_p$ values. I am indebted to Drs. Larson and Dodge for this equation. Since a certain error is involved in the use of this equation when the volume fraction of ammonia, $a$, is large, I have made a separate study of the high pressure data, using exactly calculated values of $K_p$. The same conclusions follow. The representation of the data by the surface, which now has slightly different coefficients, is not quite so good, but nearly so. The important discrepancy is in no way lessened. It was obviously unnecessary to repeat the low pressure calculations, since the error becomes much smaller.

examined. A similar discontinuity exists between the given data at 30 atmospheres and Haber's data at the same pressure. Both discontinuities are believed to be the result, not of experimental error, but of variation in the composition of the gas mixture.

4. Evidence is therefore found in the data for the Haber equilibrium that the function $K_p$ is not strictly constant with respect to any variation whatsoever of the internal variables, the number of independent variables being given by the phase rule.

5. An important experimental task, therefore, remains; to determine, at least around the stoichiometrical composition, the variation of $K_p$ with the composition. At high pressures the maximal yield of ammonia may occur at a hydrogen-nitrogen ratio different from three.

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## The Activities of Strong Electrolytes

## I. The Activity of Hydrochloric Acid Derived from the Electromotive Force of Hydrogen-Silver-Chloride Cells

by

George Scatchard

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[Contribution from the Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology, No. 164]

# THE ACTIVITIES OF STRONG ELECTROLYTES. I. THE ACTIVITY OF HYDROCHLORIC ACID DERIVED FROM THE ELECTROMOTIVE FORCE OF HYDROGEN–SILVER-CHLORIDE CELLS[1]

By George Scatchard[1a]

Received July 9, 1924 Published March 5, 1925

## Introduction

As a preliminary to a study of liquid-junction potentials and of the effect of non-electrolytes on the activities of ions, a series of measurements has been made of the electromotive force of hydrogen–hydrochloric-acid–silver-chloride cells, and the mean activity coefficients of the ions have been calculated from them and earlier measurements on the same type of cells. These values differ markedly from those computed by Lewis and Randall.[2]

The electromotive force of the cell, Pt,$H_2$ | HCl,HgCl | Hg, has been measured by Ellis[3] and by Linhart.[4] These measurements do not extend to dilute enough solutions to permit the calculation of the activities from them alone, and the discrepancy between different comparisons of the calomel and silver chloride electrodes[5] makes their correlation with the latter uncertain. They have not been used in this paper.

Noyes and Ellis[6] and Linhart[7] have measured the electromotive force of the cell, Pt,$H_2$ | HCl,AgCl | Ag, in dilute solutions. These measurements have now been extended through the concentration range 0.01–1.5 *M*.

## I. Experimental Procedure

Conductivity water from the still in this Laboratory was used throughout. The solutions of hydrochloric acid were prepared by dilution of a constant-boiling mixture, the late middle fraction of the distillation from c. p. hydrochloric acid diluted with about two parts of water. The acid content of the constant-boiling acid was determined by a chloride analysis, and always checked the value given by Hulett and Bonner[8] within 0.1%. All weights were reduced to vacuum standard.

The hydrogen was prepared from a cell containing 25% sulfuric acid as electrolyte, with zinc amalgam, prepared with c. p. zinc, as one electrode and a large sheet of platinized platinum as the other. This provides a very convenient source of small amounts of hydrogen. The gas was passed over copper reduced from the oxide and heated to about 300°, then through water and finally through a wash bottle at 25° which contained the same solution as that in the electrode vessels.

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[1] Revised copy received December 11, 1924.

[1a] National Research Fellow.

[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 336.

[3] Ellis, This Journal, **38**, 737 (1916).

[4] Linhart, *ibid.*, **39**, 2601 (1917).

[5] Ref. 2, p. 407, Note 5.

[6] Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[7] Linhart, *ibid.*, **41**, 1175 (1919).

[8] Hulett and Bonner, *ibid.*, **31**, 390 (1909).

The hydrogen electrodes were made of platinized platinum sheet about 1 × 0.5 cm. The silver chloride electrodes were of platinum gauze of the same size, plated with silver and then chloridized electrolytically in the solution in which they were to be used, according to the directions of MacInnes and Beattie.[9] The electrodes were used within one to three days after preparation. The agreement between two solutions of approximately the same concentration, and between these results and those of Linhart,[7] who used precipitated silver chloride, gives good justification for the use of electrolytic silver chloride prepared in this way.

The work was planned as a preliminary to a study of solutions containing sugar or other non-electrolytes, in which it is necessary to attain equilibrium rather rapidly. The hydrogen cell, therefore, is a modification of the Clark rocking electrode,[10] simplified somewhat by the absence of a liquid junction, and designed for use in a water thermostat. The design of the apparatus, which was made of Pyrex glass, is given in Fig. 1. It has the disadvantage that the solution comes in contact with two rubber stoppers and the rubber tube connecting the electrode vessels. The rubber, however, was boiled with sodium hydroxide solution, then with hydrochloric acid, and finally with water, and there was no indication of any difficulty from this source, unless this is the explanation of the slight divergence of my values from that of Linhart in the 0.01 *M* solution. The rocking device is so designed that the joint between the rubber tubing and the hydrogen electrode vessel is nearly in the axis of rotation, and the rubber stopper in this vessel is directly below that axis. The vessels were immersed in a water thermostat at 25 ± 0.02°.

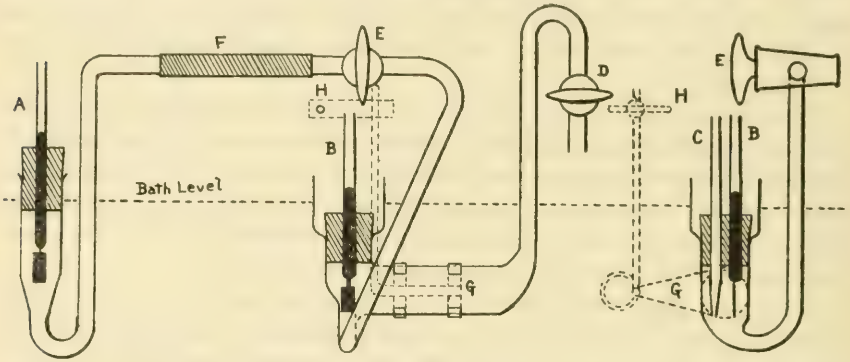

Fig. 1.—A, Silver chloride electrode; B, Hydrogen electrode; C, Hydrogen inlet; D, Stopcock at outlet; E, Stopcock to separate half-cells; F, Flexible rubber connection; G, Clamp; H, Axis of rotation. Scale, 1:3.

The potentiometer was a Leeds and Northrup, Type K instrument. The standard Weston cell was checked during the course of the investigation against two others newly calibrated by the Bureau of Standards.

Six silver chloride electrodes were prepared together, all of which, generally, agreed in electromotive force within 0.02–0.03 mv. The average value was determined, discarding any electrode which differed more than 0.03 millivolt from the average of the others. The electrode nearest this value was used, and correction was made to the average when necessary.

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[9] MacInnes and Beattie, This Journal, 42, 1132 (1920).

[10] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, 1923, pp. 181–185.

After the electrodes and electrode vessels were rinsed, the vessels, including the glass hydrogen inlet, were completely filled with the solution. When hydrogen had been evolved long enough to displace any air from the pre-saturator and tube, the hydrogen train was connected. With the hydrogen vessel rocked about two-thirds forward, the solution was displaced with hydrogen until gas escaped from Stopcock D. The apparatus was rocked for five minutes. With the vessel rocked completely back, hydrogen was bubbled in long enough to displace all that in the apparatus; the apparatus was rocked for another five minutes. This was done five times before any measurement was made. Before each measurement

TABLE I

ELECTROMOTIVE FORCE IN MILLIVOLTS OF CELLS Pt, $H_2$ | HCl, AgCl | Ag

| Molality $m$ | $E$ measured | Mean dev. from av. | $E_0'$ $E + 118.3 \log m$ | Difference from curve |
|---|---|---|---|---|
| 0.01002 | 463.76 | 0.01 | 227.30 | −0.13 |
| .01010 | 463.31 | .08 | 227.21 | − .27 |
| .01031 | 462.28 | .04 (2) | 227.23 | − .27 |
| .04986 | 385.82 | .03 | 231.77 | − .03 |
| .05005 | 385.68 | .04 | 231.82 | + .02 |
| .09642 | 353.93 | .04 | 233.76 | − .15 |
| .09834 | 353.16 | .01 (2) | 234.00 | + .02 |
| .2030 | 317.74 | .03 | 235.82 | .00 |
| .3063 | 293.32 | .03 | 236.53 | .00 |
| .3981 | 284.07 | .03 | 236.75 | .00 |
| .5009 | 271.97 | .07 | 236.44 | .00 |
| .5013 | 271.95 | .02 | 236.47 | − .02 |
| .6367 | 259.02 | .06 | 235.83 | .00 |
| .9377 | 236.96 | .02 | 233.65 | + .04 |
| 1.0008 | 232.90 | .05 | 232.94 | − .04 |
| 1.5346 | 205.34 | .08 | 227.34 | .00 |
| | | LINHART | | |
| 0.000136 | 680.5 | | 223.1 | − .1 |
| .000242 | 651.4 | | 223.6 | + .1 |
| .000483 | 616.1 | | 223.8 | .0 |
| .001000 | 579.1 | | 224.2 | − .2 |
| .004826 | 500.2 | | 226.2 | .0 |
| .00965 | 465.8 | | 227.4 | .0 |
| .04836 | 387.4 | | 231.7 | .0 |
| | | NOYES AND ELLIS | | |
| .000999 | 578.93 | | 223.98 | − .36 |
| .003378 | 516.96 | | 224.60 | −1.07 |
| .00948 | 466.66 | | 227.32 | +0.08 |
| .03324 | 405.45 | | 230.56 | .00 |
| .09534 | 354.53 | | 233.78 | − .10 |
| .33314 | 293.48 | | 237.02 | + .44 |

Stopcock D was opened momentarily to equalize the pressure. The readings were continued, after each addition of hydrogen and rocking, until three successive ones agreed within 0.02 mv. Generally, the last two were in exact agreement. This required from three to seven readings. The final value never differed from the first reading as much as 0.1 mv.

The measurement was then repeated with the same silver chloride electrode but another hydrogen electrode. The next day similar measurements were made with another silver chloride electrode, with one of the same hydrogen electrodes, and with a third hydrogen electrode, so that four measurements were made on each solution. Table I contains the results of these experiments, together with those of Linhart and of Noyes and Ellis.

The first column gives the concentration; the second, the measured electromotive force in millivolts, corrected in all cases to one atmosphere partial pressure of hydrogen. The third column gives the mean deviation of the four determinations from their average; in the two cases where (2) follows this column, only two determinations were made.

### Calculation of Activity Coefficients from Electromotive-Force Measurements

For the calculation of activity coefficients from electromotive-force measurements, Lewis and Randall define the quantity $E_0'$ by the equations: $E_0' = E + 118.3 \log m = E_0 - 118.3 \log \gamma$, where $E$ is the measured electromotive force, and $E_0$ the value of $E_0'$ at zero concentration, all in millivolts; $\gamma$ is the mean activity coefficient of the ions. The fourth column of Table I contains the values of $E_0'$ calculated from the experiments.

The values of $E_0'$ calculated from the above measurements were plotted against $\sqrt{m}$ on a large scale, and a smooth curve drawn through them. To extrapolate to zero concentration, the curve was made asymptotic to a straight line with slope $59.15\sqrt{m}$.[11] The deviations of the experimental points from the smooth curve are given in the fifth column of Table I. Except for a few points of Noyes and Ellis these deviations are very small. Linhart's values and mine agree exactly at 0.05 $M$. At 0.01 $M$, where there is a discrepancy of 0.2 mv., his value is taken as correct (although he made but one measurement compared to my three at this point) because my apparatus was not designed for work on very dilute solutions.

The agreement of Linhart's results in dilute solutions is remarkable and gives strong confirmation of the equation of Debye and Hückel. It should be noted that Linhart himself, followed by Lewis and Randall, discarded his measurement on the most dilute solution because it did not fit his method of extrapolation.

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[11] This corresponds to the asymptotic limiting law, $\log \gamma = 0.5\sqrt{m}$, of the theory of Debye and Hückel. A discussion and justification of this equation is given in the second paper of this series.

The values of the mean activity coefficients of the ions of hydrochloric acid calculated from the above curve at rounded concentrations ($\gamma_{25}$, e.m.f.) are given in the fifth column of Table II. The values of Lewis and Randall ($\gamma_{25}$, L and R) are given in the second column. The difference between the two series is due to the different values for $E_0'$ through the minimum, where their series is based on a few not very accurate measurements, and at zero concentration, where they use 223.4 and I find 222.6 mv. The two differences tend to compensate in the more concentrated solutions.

TABLE II

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID

| Molality | $\gamma_{25}$ | $\gamma_0$ Freezing point | | $\gamma_{25}$ |
|---|---|---|---|---|
| | L and R | R and V | S | E.m.f. |
| 0.001 | 0.984 | 0.973 | 0.966 | 0.966 |
| .002 | .971 | .962 | .953 | .954 |
| .005 | .947 | .940 | .930 | .932 |
| .01 | .924 | .916 | .907 | .910 |
| .02 | .894 | .884 | .879 | .881 |
| .05 | .860 | .840 | .836 | .836 |
| .1 | .814 | .809 | .804 | .801 |
| .2 | .783 | (.782) | | .774 |
| .3 | .768 | | | .763 |
| .4 | .763 | | | .760 |
| .5 | .762 | | | .763 |
| .6 | .770 | | | .770 |
| .75 | .788 | | | .783 |
| 1.0 | .823 | | | .817 |
| 1.5 | | | | .905 |

## Calculation of Activity Coefficients from Freezing-Point Measurements

Since this paper was originally submitted for publication, Randall and Vanselow[12] have published a series of very accurate freezing-point measurements on dil. hydrochloric acid and have calculated activity coefficients from them. From these coefficients and the electromotive force measurements in the more concentrated solutions, they find a value of 223.0 mv. for $E_0$ of the hydrogen–silver-chloride cell. From their data it is possible to compute $E_0'$ at any concentration.

The deviations in millivolts of Linhart's measurements from the curve of Randall and Vanselow are, in order of increasing concentrations, −0.4, −0.1, −0.2, −0.25, +0.1, 0.0, −0.15. In Fig. 2 are given the experimentally determined values of $E_0'$ up to 0.05 $M$ plotted against $\sqrt{m}$. The upper full line is the rectilinear asymptote with slope 59.15 $\sqrt{m}$, the lower full line is the curve determined from the electromotive-force measurements, and the dotted line is the curve calculated from Randall and Vanselow's data. It is obvious that the full line fits Linhart's experimental data much better than the dotted curve. It is not impossible, however, that the deviations are within the experimental error of his observations.

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[12] Randall and Vanselow, THIS JOURNAL, 46, 2418 (1924).

It is certain that the deviations are within the experimental error of the freezing-point determinations. Randall and Vanselow represent the values of $j$ (one minus the ratio of the molal freezing-point depression to the molal depression at zero concentration) up to 0.01 $M$ by the equation,

$$j = 0.316\, m^{0.513} \tag{1}$$

They also show that the $j$ values can be satisfactorily represented through the same range by the equation, $j = 0.302\, m^{0.5}$, in which $m$ has the exponent 0.5 required by the simple Debye-Hückel equation, but in which the coefficient is smaller than the value required by their theory. It seems also of interest to show that they can be represented by an equation of the form required by the Debye-Hückel theory when the size of the ions is considered (see the following article). Fig. 3 shows with what degree of accuracy the $j$ values are represented by the equation,

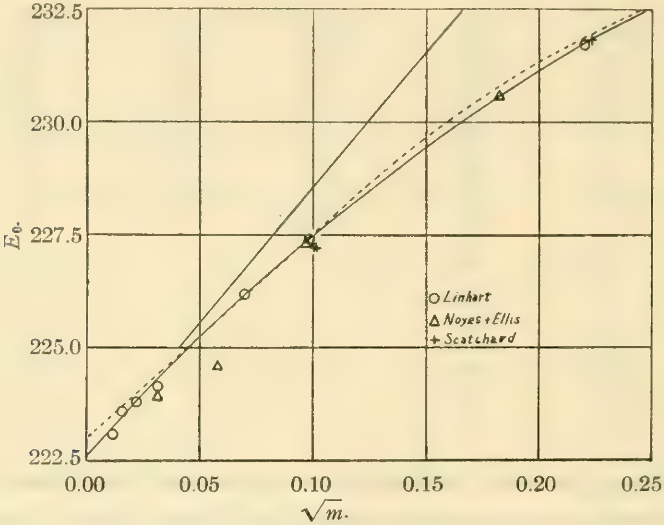

Fig. 2.—Electromotive-force measurements.

$$j = 0.38\, m^{0.5} - 0.85\, m \tag{2}$$

which gives $-\log \gamma = 0.495 \sqrt{m} - 0.738\, m$. In this figure the values of $j$ from Randall and Vanselow's paper are plotted against $\sqrt{m}$. The upper full line is the straight-line asymptote $j = 0.38 \sqrt{m}$. Up to 0.01 $M$ the dotted line is the curve of Equation 1, the lower full line that of Equation 2; at higher concentrations both curves are smooth graphic extensions of the curves at lower concentrations.

It is seen that the curve of Equation 2 does not fit the $j$ values as well as that of Equation 1; and the average deviation of the points is found to correspond to 0.00017° for Equation 2 and to 0.00010° for Equation 1. However, between 0.003 and 0.01 $M$ the difference between duplicate conductivity measurements is 0.10–0.15%, which corresponds to one-half to three-quarters of the maximum difference between the two curves. (The diameters of the circles in Fig. 3 correspond to 0.10%.) Through this range the smoothed molal conductance values of Randall and Vanselow correspond closely to the minimum $j$ values. With the use of values that appear to me to give the best smoothing, Equation 2 fits the data slightly better than Equation 1. In spite of the apparent discrepancy between $\sqrt{m} = 0.1$ and 0.2, the agreement of the data with the two curves above $\sqrt{m} = 0.1$ is practically the same, and in both cases within the experimental error.

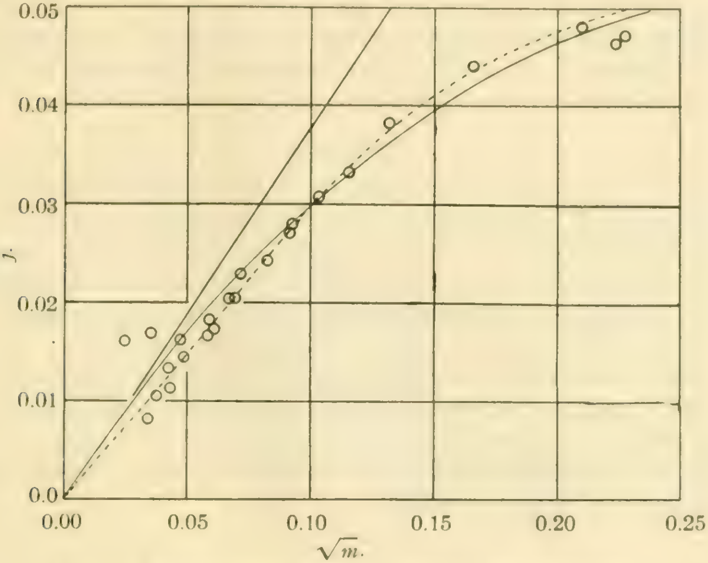

Fig. 3.—Freezing points of HCl. (Randall and Vanselow.)

The values of the activity coefficients calculated from Equations 1 and 2 are given in the third and fourth columns of Table II. Above 0.01 $M$, both the determination of $j$ and the computation of $\gamma$ are performed graphically. On the average the coefficients from Equation 1 are 0.6% greater than those from electromotive-force measurements, those from Equation 2 are 0.1% less. It is apparent that these latter values together with $E_0$ = 222.6 mv. would give a curve in Fig. 2 almost identical with that from the electromotive-force measurements.

The agreement of the values computed from the freezing-points by either formula with those from the electromotive-force measurements is very good, and the activity coefficients of the ions of hydrochloric acid can be considered to be determined within a few tenths of a per cent. It seems clear that the freezing-point measurements cannot determine the activity coefficient more closely than the difference between the results required by Equations 1 and 2. The values computed from electromotive-force measurements lie within this range and determine the most probable values still more accurately.

In conclusion I wish to express my gratitude to the National Research Council for its financial assistance, and to Professor F. G. Keyes and the other members of the staff of this Laboratory, especially to Professor D. A. MacInnes, for the suggestions and help they have given.

## Summary

1. The electromotive force at 25° of the cell, $Pt,H_2 | HCl,AgCl | Ag$, has been measured at several concentrations in the range 0.01–1.5 *M*, using a rocking hydrogen-electrode vessel designed for use in a water thermostat.

2. The mean activity coefficients of the ions have been calculated from these measurements and earlier ones on the same type of cells.

3. The coefficients are in very good agreement with those calculated from the freezing-point measurements of Randall and Vanselow.

4. The resulting activity coefficients at low concentrations are consistent within the experimental error with the limiting equation of Debye and Hückel, retaining the theoretical value of the constant of that equation.

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## The Activities of Strong Electrolytes.
## II. A Revision of the Activity Coefficients of Potassium, Sodium, and Lithium Chlorides, and Potassium Hydroxide

by

George Scatchard

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# THE ACTIVITIES OF STRONG ELECTROLYTES. II. A REVISION OF THE ACTIVITY COEFFICIENTS OF POTASSIUM, SODIUM, AND LITHIUM CHLORIDES, AND POTASSIUM HYDROXIDE[1]

By George Scatchard[1a]

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## I. Introduction

For a study of liquid-junction potentials, to be published later, values for the mean activity coefficient of the ions of potassium chloride more accurate than those available in the literature were necessary. In an attempt at accurate revision the activity coefficients of the salts named in the title were calculated from all available measurements of electromotive force, freezing point and vapor pressure.

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[1] Revised manuscript received December 11, 1924.

[1a] National Research Fellow.

The methods of computation are essentially those of Lewis and Randall[2] except for the extrapolation to zero concentration, which was in accordance with the theory of Debye and Hückel.[3] This theory expresses the variation from the laws of an ideal solution due to the electrical charges on the ions. If Raoult's law be taken as the ideal, the equation may be written

$$-\log \frac{a_{\pm}}{55.5\ N} = \frac{Aw\sqrt{c}}{1 + \alpha\sqrt{c}} \qquad (1)^{4}$$

where $a_{\pm}$ is the mean activity of the ions so expressed as to approach the molality ($m$) at zero concentrations, $N$ is the mole fraction, $A$ is a constant depending on the medium and temperature, $w$ is another constant depending on the valence type of the salt (for uni-univalent electrolytes it is unity), $\alpha$ is a constant for each salt depending on the mean diameter of the ions, and $c$ is the concentration in moles per liter.

For dilute aqueous solutions this equation may be simplified by expanding to a power series in $c$ and neglecting powers higher than the first, by giving $A$ the value 0.5 at all temperatures, and by ignoring the small differences between 55.5 $N$, $c$ and $m$. The equation may be written

$$-\log \frac{a_{\pm}}{c} = 0.5w\sqrt{c} - Bc \qquad (2)$$

or

$$-\log \gamma = -\log \frac{a_{\pm}}{m} = 0.5w\sqrt{m} - Bm \qquad (3)^{5}$$

Equation 3 has been used in this paper: at zero concentration it approaches

$$-\log \gamma = 0.5w\sqrt{m} \qquad (4)$$

For freezing-point measurements it is convenient to use the quantity $j = 1 - \dfrac{\theta}{1.858\ \nu m}$, where $\theta$ is the freezing-point depression and $\nu$ is the number of ions formed from one molecule of salt. The equation corresponding to (3) is

$$j = 0.38w\sqrt{m} - bm \qquad (5)$$

which gives,

$$-\log \gamma = 0.495w\sqrt{m} - 0.868bm \qquad (6)$$

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[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, Chapters 26–28.

[3] (a) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). (b) Debye, *ibid*., **24**, 334 (1923). (c) Hückel, *Ergebnisse exact. Naturwiss.*, **3**, 199 (1924).

[4] An equivalent form of the equation is given in Ref. 3 c; the original statement in 3 a gave the less accurate form using $a_{\pm}/c$.

[5] $B = \alpha A w$. The value of $B$ determined experimentally also includes deviations from the simple Equation 1. Two possible causes for deviations approximately proportional to the concentration are ionic hydration [Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920)], and changing dielectric constant with changing concentration (Huckel, not yet published).

Lewis and Linhart[6] and Lewis and Randall use the equation

$$j = \beta m^{\alpha} \tag{7}$$

which gives

$$-\log \gamma = \beta' m^{\alpha} \tag{8}$$

Equations 5 and 7 may be compared by taking the logarithms:

$$\log j = 0.5 \log m + \log (0.38\, w - b\sqrt{m}) \tag{5'}$$

and

$$\log j = \alpha \log m + \log \beta \tag{7'}$$

Equation 7 is claimed to be valid only up to 0.01 $M$, and the error in determining $j$ is very large below 0.003 $M$. Through the range 0.003–0.01 $M$, Equations 5 and 7 may both fit the experimental data. If $b$ is small $0.38w - b\sqrt{m}$ will be nearly constant, $\alpha$ will equal 0.5 but $\beta$ will be less than 0.38 $w$. This is the case with all uni-univalent electrolytes studied and with lead nitrate. For the complex salts used in the solubility measurements of Brönsted and La Mer,[7] $b$ is so small that the difference between $\beta$ and 0.38 $w$ is not measurable up to 0.01 $M$.

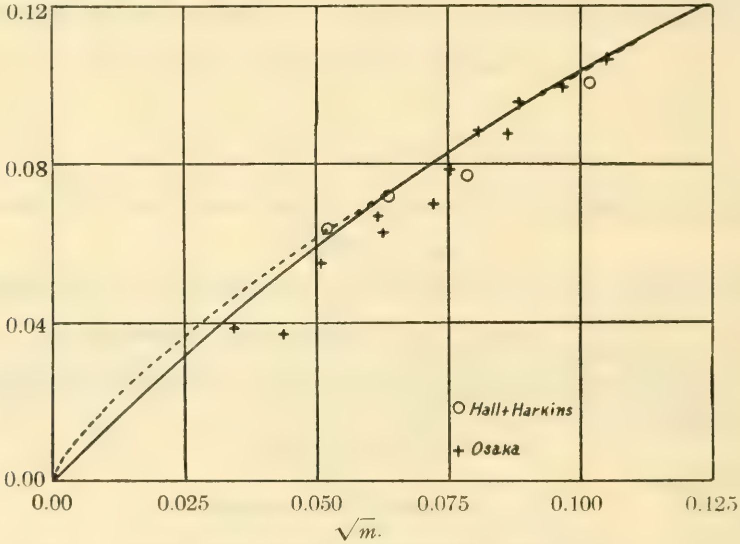

Fig. 1.—Potassium sulfate freezing points.

If $b$ is large the variation in $0.38w - b\sqrt{m}$ will appear in Equation 7 as a value for $\alpha$ less than 0.5. This happens with most salts of higher valence types where $w$ and $b$ are both large. Fig. 1 shows the values of $j$ for potassium sulfate, upon which the most accurate measurements have been made. The circles are the experimental points of Hall and Harkins,[8] the crosses those of Osaka.[9] The full line represents the equation $j = 1.316\sqrt{m} - 2.8m$, the dotted line $j = 0.572m^{0.374}$. · Through the range of experimental test the two equations are almost identical, although they deviate considerably at both lower and higher concentrations.

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[6] Lewis and Linhart, THIS JOURNAL, **41**, 1952 (1919).

[7] Brönsted and La Mer, *ibid.*, **46**, 555 (1924).

[8] Hall and Harkins, *ibid.*, **38**, 2658 (1916).

Similarly the freezing-point data for all the salts discussed by Lewis and Randall may be represented within their apparent experimental error by Equation 5. The data for potassium and sodium chlorides are discussed later in this paper. The measurements of Randall and Vanselow[10] on hydrochloric acid have already been discussed.[11] Their measurements on thallous chloride and lead nitrate fit Equation 5 with $b = 1.0$ and $1.034$, respectively, almost exactly as well as they do Equation 7 with the constants given by the authors.

Noyes[12] concludes that by giving to the constant in Equation 4 a value about five-sixths of that demanded by the theory of Debye and Hückel, values of the activity coefficients are obtained which are in better agreement with the experimentally derived values. This conclusion, however, is based on the use of the simple equation even up to 0.1 or 0.2 $M$, and by comparison with values many of which are derived through extrapolations by means of Equation 8. The Debye-Hückel theory demands that, if the ions have molecular dimensions, the deviations from Equation 4 shall be evident at approximately 0.001 $M$.

In view of the discrepancy between the equation of Milner and that of Debye and Hückel, I should base the justification of Equations 3 and 5 upon the electromotive-force measurements of Linhart with hydrochloric acid, and especially upon the solubility measurements of Brönsted and La Mer.[7] Both indicate clearly a value for $A$ not greatly different from 0.5. Greater experimental accuracy in the future may justify the use of a more accurate form of the equation even in dilute solutions. At present there are no experimental data which are not fitted within their experimental error by Equation 3 up to 0.01 $M$, and none on uni-univalent electrolytes other than hydrochloric acid for which the equation does not hold up to 0.1 $M$.

## II. Potassium Chloride

**A. Calculation from Electromotive-Force Measurements.** The electromotive force of the cell, $Ag \mid AgCl,KCl(c') \mid K,Hg \mid KCl(c''),AgCl \mid Ag$, has been measured at 25° by MacInnes and Parker[13] with the solution pairs 0.005–0.05, 0.01–0.1 and 0.05–0.5 $M$, and by Beattie[14] with 0.1-

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[9] Osaka, *Z. physik. Chem.*, **41**, 560 (1902).

[10] Randall and Vanselow, *ibid.*, **46**, 2418 (1924).

[11] Scatchard, *ibid.*, **47**, 641 (1925).

[12] Noyes, *ibid.*, **46**, 1080, 1098 (1924).

[13] MacInnes and Parker, This Journal, **37**, 1445 (1915).

[14] Beattie, *ibid.*, **42**, 1130 (1920).

1.0 $M$. Because of difficulties in exactly duplicating the amalgam concentration, no attempt was made to measure the half-cells alone. So $E_0'$ ($E_0' = E + 118.3 \log m = E_0 - 118.3 \log \gamma$, where $E$ is the measured electromotive force, $E_0$ is the value of $E_0'$ at zero concentration and $\gamma$ is the mean activity coefficient of the ions) cannot be calculated directly, but only differences between its values in different solutions. Moreover, the second cell of MacInnes and Parker is not correlated with the other two, so we have the problem of fitting together two overlapping series of three points each.

The procedure was to give an arbitrary value to $E_0'$ for one solution, to calculate from this its value in the other solutions of that series, to plot these $E_0'$ values against $\sqrt{m}$, to draw through them a curve approaching the slope 59.15 asymptotically with decreasing concentration, to fit the points of the second series to this curve, and to draw a smooth curve through all the points. This curve was then tested to see if the deviation from the linear asymptote was proportional to the molality in accordance with Equation 3. If it was not, a new value of $E_0$ was tried, shifting the relative position of the two series if necessary. The final curve fits the two cells with the more concentrated solutions exactly. For the other two the deviations are 0.5 and 0.8 mv. in the direction which would indicate a steeper slope than that of Equation 3. At least part of this discrepancy is probably due to the fact that the measurements of MacInnes and Parker antedate some of the improvements in technique both with silver chloride and with the amalgam electrodes.

Since the transference numbers of potassium chloride in dilute solutions are accurately known, it is possible to utilize the measurements of MacInnes and Parker[13] at 25° and of Jahn[15] at 18° on cells with transference, Ag | AgCl,KCl($c'$) | KCl($c''$),AgCl | Ag. The ratio of the electromotive force of the cell with transference to that without is 0.496 at 25° and $0.496 \times 291/298$ at 18° (making in the latter case the very reasonable assumption that in such dilute solutions the activity coefficient does not change appreciably with this small temperature change). For the measurements of MacInnes and Parker the deviations are in the same direction and of about the same magnitude as for the cell without transference. Jahn's measurements deviate in the same direction, about 0.3 mv. on the average. This is not much greater than the difference between his two series and is probably within his experimental error. The values of the activity coefficients calculated from these measurements are given in the last column of Table I.

B. **Calculation from Freezing-Point Measurements (KCl).**—The values of $j$ calculated from the measurements of Jahn,[16] Flügel[17] and

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[15] Jahn, *Z. physik. Chem.*, **33**, 545 (1900).

[16] Jahn, *ibid.* **50**, 144 (1904); **59**, 35 (1907).

[17] Flügel, *ibid.*, **79**, 577 (1912).

Adams[18] were plotted against $\sqrt{m}$ and a smooth curve was drawn through them approaching the line $0.38\sqrt{m}$ asymptotically at zero concentration, but without further restrictions. The position of the curve is determined very largely by the points in the more concentrated solutions, but those at lower concentrations agree with the curve within their experimental error. Those of Adams fall a little below the curve, those of Flügel a little above and those of Jahn are evenly distributed about it. Fig. 2 is a small-scale reproduction of the plot.

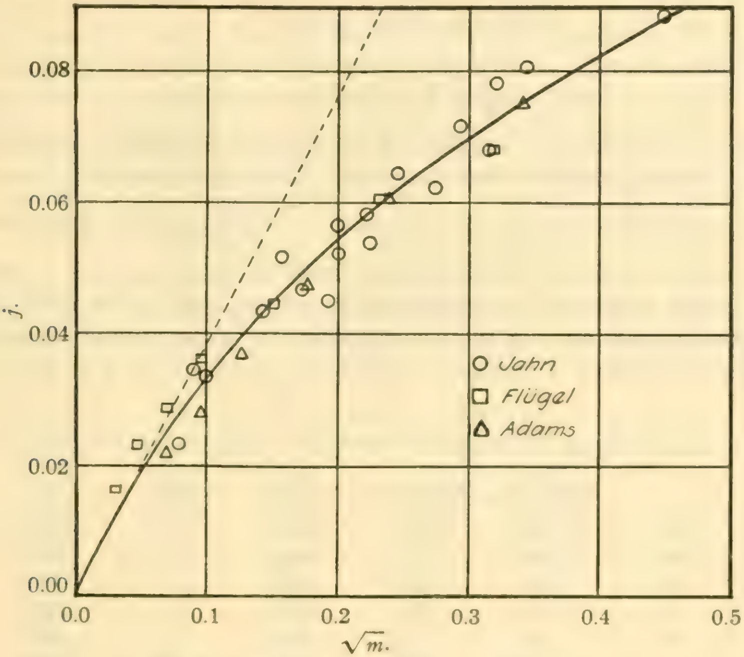

Fig. 2.—Potassium chloride freezing points.

After this curve was drawn it was found that up to 0.2 $M$ it fitted, within the accuracy of drawing, the equation $j = 0.38\sqrt{m} - 0.57m + 0.8m^2$, which gives $-\log \gamma = 0.495\sqrt{m} - 0.495m + 0.52m^2$. For the more concentrated solutions log $\gamma$ was determined by graphic integration by the method of Lewis and Randall.[2] The term in $m^2$ is regarded as simply an empirical device to fit the $j$ curve as drawn, and without theoretical significance. Below 0.1 $M$ it does not affect the value of $\gamma$ as much as 0.1%; above 0.2 $M$ it causes wide deviation from the experimental points. The values of $\gamma_0$ calculated from these measurements are given in the fourth column of Table I. By analogy to sodium chloride $\gamma_{25}$ should be a few tenths of one per cent. higher than $\gamma_0$ at 0.2 and 0.3 $M$. So the activity val-

[18] Adams, THIS JOURNAL, 37, 494 (1915).

ues from freezing points are about 1% higher than those from electromotive force. The discrepancy is not greater than the possible experimental error of either method.

**C. Calculations from Vapor-Pressure Measurements (KCl).**—Lovelace, Frazer and Sease[19] have measured the vapor pressure at 20° of aqueous potassium chloride solutions through the concentration range 0.05–4.0 *M*. The calculation of the activity coefficients from these measurements was made by the equations

$$\log \frac{a_2}{N_2} = -\int \frac{N_1}{N_2}\, \mathrm{d} \log \frac{a_1}{N_1} + C \qquad (9)^{20}$$

and

$$\log \gamma = \frac{1}{2} \log \frac{a_2}{N_2} + \frac{1}{2} \log N_2 - \log m \qquad (10)$$

where $a_1$ and $a_2$ are the activities of the solvent and solute, respectively, and $N_1$ and $N_2$ are their mole fractions. The vapor pressure of water at 20° is taken as 17.539 mm.,[21] so that $a_1 = \frac{17.539 - \Delta p}{17.539}$. The value of the constant $C$ cannot be determined from these measurements because they do not extend to low enough concentrations, and in the most dilute solutions a small error in the measurements or in the graphic integration affects the value of $\gamma$ markedly. Therefore the value of $\gamma$ in the 1.0 *M*

TABLE I

MEAN ACTIVITY COEFFICIENTS OF THE IONS OF POTASSIUM CHLORIDE

| Molality | $\gamma_{25}$ Lewis and Randall | $\gamma_{25}$ Noyes and MacInnes | $\gamma_0$ Freezing points | $\gamma_{20}$ Vapor pressures | $\gamma_{25}$ E.m.f. |
|---|---|---|---|---|---|
| 0.001 | 0.977 | 0.979 | 0.966 | | 0.965 |
| .002 | .967 | | .952 | | .951 |
| .005 | .946 | .923 | .928 | | .926 |
| .01 | .922 | .890 | .902 | | .899 |
| .02 | .892 | | .870 | | .865 |
| .05 | .841 | .790 | .818 | 0.849 | .809 |
| .1 | .796 | .745 | .772 | .789 | .762 |
| .2 | .749 | .700 | .719 | .728 | .715 |
| .3 | | .673 | .686 | .692 | .688 |
| .4 | | | | .667 | .669 |
| .5 | .682 | .638 | | .652 | .654 |
| .6 | | | | .640 | .642 |
| .75 | | | | .627 | .627 |
| 1.0 | .634 | .593 | | (.605) | .605 |
| 2.0 | | | | .574 | |
| 3.0 | | | | .569 | |
| 4.0 | | | | .580 | |

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[19] Lovelace, Frazer and Sease, THIS JOURNAL, **43,** 102 (1921).

[20] Ref. 2, Chapter 22, p. 269. Eq. 22–23 with subscripts changed.

[21] Landolt-Börnstein "Tabellen," **1912,** p. 360. The 1923 edition gives 17.535 based on the same experimental work. The difference is unimportant.

solution was taken, the same as that from the electromotive force measurements. The values for $\gamma_{20}$ so determined are given in the fifth column of Table I. Down to 0.3 $M$ the results by the two methods agree within a few tenths of one per cent.; between 0.2 and 0.05 $M$ the discrepancy increases to 4%, which is probably not beyond the errors in measurement and calculation of the vapor pressure method.

The values for the mean activity coefficients of the ions of potassium chloride given by Lewis and Randall and by Noyes and MacInnes[22] are also given in the second and third columns of Table I. My results lie between the two earlier ones but closer to those of Noyes and MacInnes. The differences all lie in the methods of extrapolation. Lewis and Randall assumed that in very dilute solutions the activity coefficients of potassium chloride are the same as the values they found for sodium chloride.

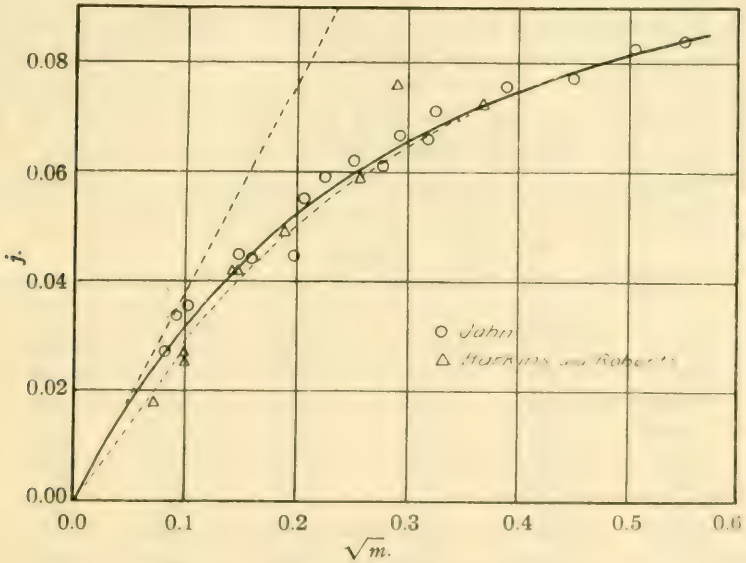

Fig. 3.—Sodium chloride freezing points.

## III. Sodium Chloride

**A. Calculation from Freezing-Point Measurements.** The method used was exactly the same as that employed for potassium chloride in Section IIB. Fig. 3 is a small-scale reproduction of the plot of the $j$ values of Jahn[16] and of Harkins and Roberts.[23] The upper dotted line is the asymptote, $j = 0.38\sqrt{m}$, the full line is the smooth curve used. Up to 0.2 $M$ it is fitted within the accuracy of drawing by the equation $j = 0.38\sqrt{m} - 0.6m + 0.7m^2$, which gives $-\log \gamma = 0.495\sqrt{m} - 0.521m +$

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[22] Noyes and MacInnes, This Journal, 42, 239 (1920).

[23] Harkins and Roberts, *ibid.*, 38, 2676 (1916).

$0.46m^2$. As in the case of potassium chloride the position of the curve is determined largely by the points at higher concentrations and the limiting law. It fits the results of Jahn for dilute solutions very well; the deviations of the measurements of Harkins and Roberts in the dilute solutions correspond to less than 0.0003°. It should be noted that Hall and Harkins,[8] and presumably Harkins and Roberts, correct "all measurements at low concentration" by 0.0001° because this was the average deviation of non-electrolytes from the ideal law, $\theta = 1.858\ m$. This correction is in the direction to decrease $j$.

The lower dotted line represents the $j$ values used by Lewis and Randall.[24] They have apparently given full weight to the measurements of Harkins and Roberts in dilute solutions. To obtain a smooth curve they have given little weight to the measurements at 0.02 $M$ ($\sqrt{m} = 0.14$), whose deviation from their curve is again nearly 0.0003°. Their curve also fits the measurements of Adams on potassium chloride better than mine does, but the deviation of his results from my curve in dilute solutions is less than 0.0002°. I believe that, taken as a whole, the experimental results for sodium chloride, like those for potassium chloride, are fitted better by my curve than by that of Lewis and Randall. Certainly, neither offers important evidence for preference of Equation 7 to Equation 5 for extrapolation, or for a change in the value of the constant $A$.

Table II

Mean Activity Coefficients of the Ions of Sodium Chloride

| Molality | $\gamma'$ Lewis and Randall | $\gamma'$ Scatchard | Ratio $\gamma'_S/\gamma'_{L+R}$ | $\gamma_{25}$ Lewis and Randall | $\gamma_{25}$ Scatchard |
|---|---|---|---|---|---|
| 0.001 | 0.977 | 0.966 | 0.989 | 0.977 | 0.966 |
| .002 | .967 | .953 | .985 | .967 | .953 |
| .005 | .946 | .928 | .981 | .946 | .928 |
| .01 | .922 | .903 | .979 | .922 | .903 |
| .02 | .892 | .871 | .977 | .892 | .871 |
| .05 | .842 | .821 | .975 | .842 | .821 |
| .1 | .798 | .778 | .975 | .798 | .778 |
| .2 | .750 | .732 | .976 | .752 | .734 |
| .3 |  | .703 |  |  |  |
| .5 | .682 |  |  | .689 | .671 |
| 1.0 | .630 |  |  | .650 | .634 |
| 2.0 | .613 |  |  | .661 | .645 |
| 3.0 | .627 |  |  | .704 | .686 |
| 4.0 | .657 |  |  | .765 | .746 |
| 5.0 | .713 |  |  | .852 | .831 |
| 5.2 | .729 |  |  | .874 | .852 |

Between 0.05 and 0.2 $M$, the ratio of $\gamma'$ calculated by Lewis and Randall and by me is constant within 0.1%. For the more concentrated solutions I have taken their values of $\gamma'$ multiplied by the factor 0.975. Through-

out I have used their values for the ratio $\gamma_{25}/\gamma'$. Table II contains the values of $\gamma'$ calculated by Lewis and Randall and by me, the ratio of these two, and the values of $\gamma_{25}$ calculated from the two values of $\gamma'$.

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[24] Ref. 2, p. 348.

**B. The Electromotive Force Measurements (NaCl).**—Allmand and Polack[25] have measured the electromotive force at 25° of the cell, Hg,Na | NaCl,HgCl | Hg, with various concentrations of sodium chloride. They tell of no precautions to eliminate oxygen, which has a very serious effect on the amalgam electrodes, and it appears from the description of their procedure that oxygen must have been present. It is probably a consequence of this that their measurements on dilute solutions give results far different from any other determinations of activity, and indicating a curve much steeper than that for Equation 5. Between 0.1 and 3.2 *M* the average value of the deviation from the curve for $\gamma$ determined from freezing points is 1.2% (of $\gamma$), but there is a trend of 3.5% in these values. Since the results in dilute solutions show a deviation so much greater, it is probable that this deviation may be attributed to experimental error and that these measurements are not sufficiently accurate for the calculation of activity coefficients.

## IV. Lithium Chloride

**A. Calculation from Electromotive-Force Measurements.**—MacInnes and Beattie[26] have measured the electromotive force at 25° of the cell, Ag | AgCl,LiCl($c'$) | Li,Hg | LiCl($c''$),AgCl | Ag, over a wide range of concentration. The treatment of their data in this paper is the same as that of the similar potassium chloride cells in Section IIA, except that a larger number of points are more accurately determined and so linked together that it is only necessary to select arbitrarily one value of $E_0'$, which cancels out in the calculation of $\gamma$. The deviations of the experimental points from the curve are much smaller than for potassium chloride. Down to 0.1 *M* they do not exceed 0.03 mv.; from 0.003 to 0.1 *M* they average 0.2 mv. For the cell 0.001–0.01 *M* the deviation is 0.8 mv., probably due to the formation of lithium hydroxide from the lithium of the amalgam. Their measurements on cells with transference cannot be utilized because there are no independent measurements of the transference numbers of sufficient accuracy. The values of $\gamma_{25}$ calculated from these measurements are given in the last column of Table III.

**B. Calculation from Freezing-Point Measurements (LiCl).**—The freezing points of lithium chloride solutions have been measured by Loomis[27] and by Jahn.[16] The measurements are not very accurate and do not agree well among themselves, with Equation 5, or with the electromotive force measurements, all of which can probably be attributed to errors in the freezing-point measurements. The mean activity coefficients calculated from their measurements by the method used for potassium and sodium chlorides are given in the second column of Table III.

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[25] Allmand and Polack, *J. Chem. Soc.*, **115**, 1020 (1919).

[26] MacInnes and Beattie, This Journal, **42**, 1123 (1920).

[27] Loomis, *Ann. Physik*, **60**, 523 (1897).

**C. Calculation from Vapor-Pressure Measurements (LiCl).**—The vapor pressure of aqueous lithium chloride solutions at 20° has been measured by Lovelace, Bahlke and Frazer[28] in the concentration range 0.1–1.0 *M*. The calculation of the activity coefficients from their data is the same as the corresponding calculation for potassium chloride in Section IIC; the results are given in the third column of Table III. In dilute solutions the agreement with the results for electromotive force is better than for potassium chloride. The differences of less than 1% in the more concentrated solutions may very possibly be due to the temperature variation of $\gamma$.

TABLE III

MEAN ACTIVITY COEFFICIENTS OF THE IONS OF LITHIUM CHLORIDE

| Molality | $\gamma_0$ Freezing point | $\gamma_{20}$ Vapor pressure | $\gamma_{25}$ E.m.f. |
|---|---|---|---|
| 0.001 | 0.96 | | 0.965 |
| .002 | .95 | | .952 |
| .005 | .93 | | .927 |
| .01 | .91 | | .901 |
| .02 | .89 | | .869 |
| .05 | .85 | | .819 |
| .1 | .81 | 0.791 | .779 |
| .2 | .78 | .756 | .750 |
| .3 | .77 | .739 | .739 |
| .4 | | .732 | .735 |
| .5 | | .731 | .736 |
| .6 | | .734 | .738 |
| .75 | | .740 | .743 |
| 1.0 | | (.754) | .753 |
| 3.0 | | | 1.165 |

## V. Potassium Hydroxide

The cell, $Pt,H_2 \mid KOH(c') \mid K,Hg \mid KOH(c'') \mid H_2,Pt$, has been measured at 25° by Knobel,[29] who interpreted it as measuring directly the activity of the potassium hydroxide. However, the cell reaction must be $\frac{1}{2}\ H_2 + KOH = H_2O + K$, so that the net effect of passing a faraday of electricity through the cell is to transfer one mole of potassium hydroxide from the first cell to the second and one mole of water in the reverse direction. The electromotive-force equations are, $E = \frac{RT}{F}\ ln\ \frac{a_2'}{a_2''} - \frac{RT}{F}\ ln\ \frac{a_1'}{a_1''} = 59.15$

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[28] Lovelace, Bahlke and Frazer, THIS JOURNAL, **45**, 2930 (1923).

[29] Knobel, *ibid.*, **45**, 70 (1923).

$\log \frac{a_2'}{a_2''} - 59.15 \log \frac{a_1'}{a_1''}$, and $E_0' - E_0'' = 118.3 \log \frac{\gamma'}{\gamma''} - 59.15 \log \frac{a_1'}{a_1''}$, where the superscripts refer to the first (′) and second (″) solutions, the subscripts to the solvent ($_1$) and solute ($_2$), and the millivolt is the unit of electromotive force. The quantity $E_0' - E_0$ was calculated by the same method as that used for potassium and lithium chloride cells. In dilute solutions the effect of the activity of the water is so small that it does not alter the extrapolation to zero concentration. The curve fits the measurements within the difference between duplicate experiments.

Although there are no independent measurements of the activity of water in potassium hydroxide solutions, it may be calculated from these electromotive-force measurements by a series of approximations. For the first approximation the activity of the water was made the same as that in potassium chloride solutions at 20°. The corresponding electromotive force was added to the quantity $E_0' - E_0$ (both are negative for this type of cell), and the activity of the water was calculated from Equation 9, with subscripts changed and Equation 10. In the calculation of the activity of the solvent by this method the extrapolation to zero concentration is unambiguous. The operation was repeated using the new values of the activity of the water until the fourth repetition gave results identical to 0.01 mv. with those of the third.

Table IV

Activity of Water and Potassium Hydroxide from Concentration Cells

| Molality | $E_0' - E_0$ | Activity of water | E.m.f. due to water | $\gamma_{25}$ uncorr. | $\gamma_{25}$ corr. |
|---|---|---|---|---|---|
| 0.001 | −1.82 | 0.99996 | 0.00 | 0.965 | 0.965 |
| .003 | 3.08 | .99989 | .00 | .942 | .942 |
| .01 | 5.37 | .99963 | − .01 | .901 | .901 |
| .03 | 8.70 | .99897 | .03 | .844 | .844 |
| .1 | 13.20 | .99668 | .09 | .773 | .772 |
| .3 | 16.14 | .98988 | .26 | .730 | .727 |
| 1.0 | 14.36 | .96439 | .94 | .756 | .743 |
| 3.0 | +5.64 | .87482 | 3.42 | 1.116 | 1.044 |

In Table IV the second column gives the quantity $E_0' - E_0$ in millivolts; the third gives the activity of the water and the fourth the resulting electromotive force; the fifth column gives the values of $\gamma$ calculated without correcting for the activity of the water, the sixth column the corresponding corrected values. The correction is negligible in dilute solutions, but amounts to 7% in the 3 *M* solution. The values of $\gamma_{25}$, at rounded concentrations, are tabulated in the sixth column of Table V.

Chow[30] has measured at 25° the electromotive force of the cell, Hg | HgO,KOH($c'$) | K,Hg | KOH($c''$),HgO | Hg, which he also erroneously interpreted as giving directly the activity of potassium hydroxide. The equations for the cell reaction and for the electromotive force are $\frac{1}{2}$ Hg + KOH = $\frac{1}{2}$ HgO + $\frac{1}{2}$ $H_2O$ + K, and $E_0' - E_0'' = 118.3 \log \frac{\gamma'}{\gamma''} - 29.58 \log \frac{a_1'}{a_1''}$.

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[30] Chow, This Journal, **42,** 488 (1920).

Knobel[29] believes that Chow's results are in error for two reasons: (*a*) there was oxygen present in his cells, and (*b*) the solid mercuric oxide, due to its polymorphism, was not the same substance in the different solutions and therefore had different activities. Probably it had not always reached equilibrium. Certainly, the results of Chow differ widely from those of Knobel. The electromotive force of the cells was corrected for the activity of the water by subtracting 0.9 *m* mv., which is in accordance with Table IV up to 1.0 *M*. All the deviations are large, from 1.0 to 2.0 mv., and those in dilute solutions are in the opposite direction to those of other electromotive-force measurements.

## VI. General Discussion

For purposes of comparison, there are collected in Table V the mean activity coefficients at 25° determined from electromotive-force measurements, except those for sodium chloride which are determined from freezing points and thermal measurements. The values for hydrochloric acid are included. In Fig. 4 the same data are represented by plotting log $\gamma$ against $\sqrt{m}$. The only intersections of two curves are sodium chloride with lithium chloride and with potassium hydroxide. It is very probable that these are due to the difference in the methods of determination. It is interesting to note that the minima for hydrochloric acid,

TABLE V

MEAN ACTIVITY COEFFICIENTS OF THE IONS AT 25°

| Molality | KCl | NaCl | LiCl | HCl | KOH |
|---|---|---|---|---|---|
| 0.001 | 0.965 | 0.966 | 0.965 | 0.966 | 0.965 |
| .002 | .951 | .953 | .952 | .954 | .952 |
| .005 | .926 | .928 | .927 | .932 | .927 |
| .01 | .899 | .903 | .901 | .910 | .901 |
| .02 | .865 | .871 | .869 | .881 | .868 |
| .05 | .809 | .821 | .819 | .836 | .815 |
| .1 | .762 | .778 | .779 | .801 | .772 |
| .2 | .715 | .734 | .750 | .774 | .739 |
| .3 | .688 |  | .739 | .763 | .727 |
| .4 | .669 |  | .735 | .760 | .723 |
| .5 | .654 | .671 | .736 | .763 | .723 |
| .6 | .642 |  | .738 | .770 | .725 |
| .75 | .627 |  | .743 | .783 | .731 |
| 1.0 | .605 | .634 | .753 | .817 | .743 |

lithium chloride and potassium hydroxide all occur at about the same concentration, very near 0.4 *M*. Sodium chloride also shows a minimum between 1 and 2 *M*, and potassium chloride (at 20°) one near 3 *M*.

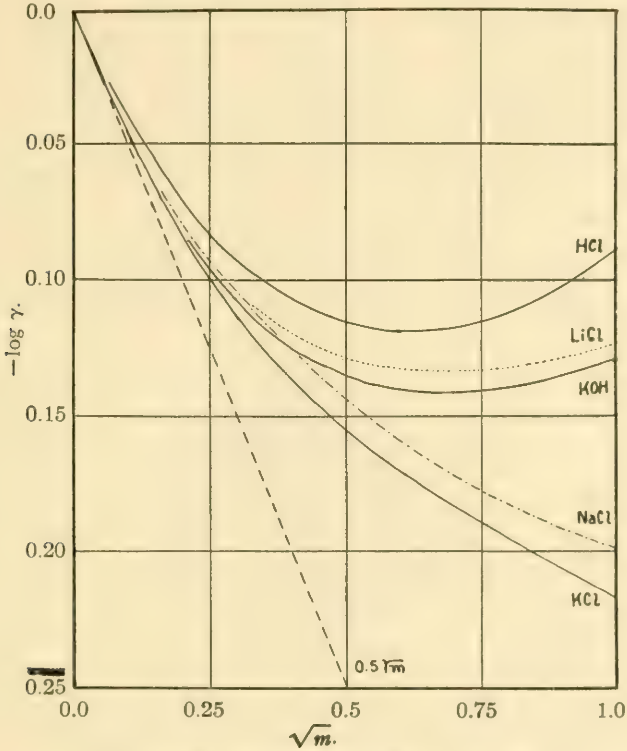

Fig. 4.—Mean activity coefficients of the ions.

## VII. Summary

1. With the use of the formula, $-\log \gamma = 0.5\sqrt{m} - Bm$, as a basis for extrapolation to zero concentration, the mean activity coefficient of the ions of the following electrolytes have been revised: potassium and lithium chlorides from electromotive force, from freezing point, and from vapor-pressure measurements; sodium chloride from freezing-point measurements; potassium hydroxide from electromotive-force measurements, taking into account the formation of water in the cell reaction.

2. The relation of the above equation to the Debye and Hückel theory of the effect of the ionic charges on the activity is discussed.

3. The equation is tested by a comparison with experimental measurements.

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## THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. III. A NOVEL FORM OF APPARATUS.

by

D. A. MacInnes and T. B. Brighton

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# THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. III. A NOVEL FORM OF APPARATUS

By D. A. MacInnes and T. B. Brighton

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The purpose of this paper is to describe an apparatus for determining transference numbers by the method of moving boundaries, in which the solutions which join at the boundaries are initially brought together by a new method. The history and theory of the determination are sufficiently described in the first paper of this series.[1] The original apparatus of Denison and Steele[2] as modified by MacInnes and Smith[1] has been found to give results of high accuracy, but it requires delicate manipulation at certain stages in the determination of a transference number. The apparatus to be described requires no special skill to operate, and for that reason the authors hope that it will prove to be useful in elementary laboratories in physical chemistry. A determination with this apparatus is more easily carried out and is far more accurate than the Hittorf method as included in most laboratory courses. The moving-boundary method is, also, very much more effective than the Hittorf method as a demonstration of the phenomena of transference and of the relative velocities of ions.

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[1] MacInnes and Smith, This Journal, **45**, 2246 (1923).

[2] Denison and Steele, *Phil. Trans.* **205A**, 449 (1906). *Z. physik. Chem.*, **57**, 110 (1906–7).

In a determination by the moving-boundary method it is necessary to bring the indicator solutions into contact with the salt solution whose transference numbers are desired in such a way as to form sharp boundaries. For a description of the way this is accomplished with the older forms of the apparatus the reader is referred to the papers mentioned above. It has occurred to us that the solutions could be brought into sharp contact by means of the mechanism outlined in Fig. 1. The electrode vessel A is fitted into the disk B, and the graduated tube D into a corresponding disk C, the disks B and C both having plane surfaces. The electrode vessel A is filled with the indicator solution and is closed with a stopper which carries the electrode. A drop of the solution, *a*, hangs from the open end of the electrode tube. (The filling can be accomplished by holding a finger over the opening until the stopper is in place, and a tighter seating of the stopper then forms the pendant drop.) The graduated tube D is filled with a slight excess of solution so that a drop *b* protrudes. Now if the disk B is slid over the disk C the excess amounts of both solutions will be sheared away and a sharp boundary will result when the tubes are in place over each other. If the solutions are properly selected and a current of electricity is caused to flow, the boundary will travel down the graduated tube D.

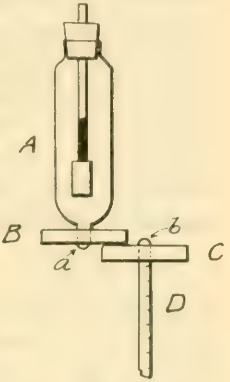

Fig. 1.

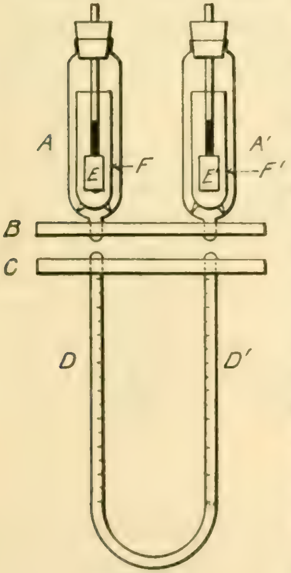

Fig. 2.

Now if two such boundaries are formed, one in which the cation of the solution under observation is followed by an indicator solution with a positive ion of lower mobility, and a corresponding boundary in which the anion is followed by an indicator solution containing a slower negative ion, the ratio of the volume swept through by either ion to the volume passed through by both ions is, with certain restrictions, the transference number. An apparatus by means of which two boundaries can be formed simultaneously is shown in Fig. 2. The electrode vessel A contains an indicator solution, of lithium chloride, for instance, and an electrode, E, which has been made of silver in all of our experiments. The vessel A′ contains the indicator solution for the negative ion and a silver-silver chloride electrode E′. The glass cups, F and F′, are put in the positions shown to keep the concentration changes around the electrodes from affecting the boundaries. The concentrated chloride solution forming around E′ during the electrolysis would otherwise sink into the graduated tube D′. The cups are provided with projections to lift them from the electrode vessels and to allow for the passage of current. The adjacent surfaces of disks B and C are lubricated with vaseline.

In addition to the determination of the transference number from the ratio of the volumes swept through, values of these constants can also be calculated from the data obtained from the movement of each boundary separately, by means of the formula[3]

$$T = \frac{F\,V}{\phi\, i\, t} \tag{1}$$

in which $V$ is the volume swept through by the boundary during the experiment, $F$ is the faraday, $\phi$ is the volume containing one gram equivalent of the salt, $t$ is the time in seconds and $i$ is the current (which must be kept constant) in amperes.

In a series of experiments in which the excess liquid in the drops was sheared off on the outer edges of the disks B and C, as shown in Fig. 1, it was found that although the ratio of the movement of one boundary to the sum of the movements of both usually gave the correct transference number, computation with Equation 1 gave values that were too low. It appeared, therefore, that all of the current was not passing through the graduated tube D-D′, some of it probably escaping through the wet streak, left in the lubricant when the boundary was formed, to the water of the thermostat in which the instrument was immersed. It was also possible that the lubricant itself was slightly conducting which would also shunt a portion of the current between the electrodes. The fact that the correct transference number may be obtained in spite of this leak would at first sight make it appear that the leak is a matter of no importance. However, as our previous work has demonstrated, it is necessary, if a boundary is to move at the theoretical rate, for the concentrations of the measured and indicator solutions to be adjusted fairly closely according to the equation,

$$C/T = C'/T' \tag{2}$$

in which $C$ and $C'$ are the concentrations of the leading and indicator solutions and $T$ and $T'$ are the corresponding transference numbers. If this is not done the correct transference number can only be obtained by compensation. The correct ratio of $C$ and $C'$ had, furthermore, been established in our determinations by previous work.

The difficulties due to electrical leak are entirely overcome and a considerable increase in the ease of manipulation gained when the disks B and

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[3] Smith and MacInnes, THIS JOURNAL, **46**, 1398 (1924).

C of the design shown in Fig. 3 are used. One of the disks is provided with a brass projection P and the other with a hole into which it fits; otherwise they are identical. A channel J forms an air insulation from the water of the thermostat when the two lubricated disks are in contact. In operation the vessels are filled as shown in Fig. 2. The disks, generously lubricated, are then placed at right angles to each other so that the pendant drops from the electrode vessels are over the depressions K and K′ (Fig. 3) on the lower disk, and the drops from the graduated tube D (Fig. 2) projecting into the corresponding spaces in the upper disk B. The apparatus is then placed in the thermostat, the level of the water coming nearly to the stoppers of the electrode vessels. Any expansions or contractions at this point due to changes of temperature will result only in slight changes in the size of the drops. The upper disk is next turned with the projection P (Fig. 3) as a center and the excess of liquid and lubricant is sheared off at the edges *a* and *a′* and at the corresponding points on the upper disk. Marks on the outer circumferences of the two disks indicate when the tubes from the electrode vessels are directly over the ends of the graduated tube. It will be noted that at this point the contacts of the two solutions are on a small plateau and are completely surrounded by air insulation so that there is no possibility of leak to the thermostat water or through the lubricant.

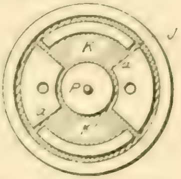

Fig. 3.

TABLE I

TRANSFERENCE NUMBERS OF 0.1 *N* POTASSIUM CHLORIDE SOLUTIONS AT 25°

| From ratio $T_{\mathrm{K}}$ | From movement of single boundaries; Equation 1 $T_{\mathrm{K}}$ | $T_{\mathrm{Cl}}$ | Sum |
|---|---|---|---|
| 0.492 | 0.492 | 0.508 | 1.000 |
| .492 | .491 | .507 | 0.998 |
| .4925 | .492 | .508 | 1.000 |
| .492 | .492 | .508 | 1.000 |
| .4915 | .491 | .507 | 0.998 |
| .492 | .491 | .507 | .998 |
| .492 | .4915 | .5075 | .999 |
| .492 | .492 | .508 | 1.000 |
| .492 | .492 | .5075 | 0.9995 |
| .4915 | .492 | .508 | 1.000 |
| .492 | .492 | .507 | 0.999 |

The success of this apparatus is best indicated by Table I, which gives the result of a series of measurements on the transference numbers of a 0.1 *N* solution of potassium chloride, at 25°. The indicator solution for the potassium ion was 0.065 *N* lithium chloride solution, and for the chloride ion 0.070 *N* potassium acetate solution. These are adjusted values established by previous investigations. The first column gives the transference number of the potassium ion from the ratios of the velocities of that ion to the velocities of both ions. The second and third columns contain values of the transference numbers computed from Equation 1. The fourth column contains the sum $T_K + T_{Cl}$ which, it will be seen, is either 1.000 or differs from that value at most by 0.2%. The agreement of the simple ratio with the values computed from Equation 1 is important since the latter values include measurements of the current, time and concentration, whereas the ratio is independent of all these factors.

In these experiments the current, about 7 ma., was kept constant by hand regulation. The current was measured by means of a potentiometer which measured the potential drop across a known resistance. The source of current was a battery of storage cells yielding about 300 volts. Of this current, 50 volts was shunted across an adjustable rheostat, the sliding contact of which was connected to the transference apparatus. Since the movement of the boundaries resulted in an increase of the resistance, movement of this sliding contact furnished the increments of potential required to keep the current constant, indication of which was obtained by observing the galvanometer in the potentiometer circuit. It is probable that the principal error in the determinations was this hand regulation of the current.[4]

A series of determinations was also made on 0.2 *N* potassium chloride solutions. Here the "adjustment" concentrations had not been determined beforehand by independent measurements. Determinations were therefore carried out in which the indicator solutions (lithium chloride and potassium acetate, as in the work described above) were varied through ranges of concentration. The results, which are given in Table II, show

TABLE II

TRANSFERENCE NUMBERS OF 0.2 *N* POTASSIUM CHLORIDE SOLUTION AT 25°

| From ratio $T_K$ | From movement of separate boundaries | | | | |
|---|---|---|---|---|---|
| | Concn. LiCl | $T_K$ | Concn. KAc | $T_{Cl}$ | Sum $T_K + T_{Cl}$ |
| 0.4915 | 0.120 | 0.490 | 0.130 | 0.507 | 0.997 |
| .486 | .123 | .490 | .142 | .518 | 1.008 |
| .491 | .125 | .490 | .135 | .508 | 0.998 |
| .490 | .125 | .489 | .137 | .509 | .998 |
| .490 | .125 | .490 | .138 | .509 | .999 |
| .490 | .125 | .489 | .139 | .509 | .998 |
| .490 | .125 | **.490** | .140 | **.510** | **1.000** |
| .490 | .125 | .491 | .141 | .510 | 1.001 |
| .489 | .125 | .491 | .142 | .513 | 1.004 |
| .489 | .127 | .492 | .145 | .514 | 1.006 |
| .471 | .130 | .493 | .150 | .553 | 1.046 |

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[4] The difficulties encountered when an attempt was made to obtain the time-current product with a coulometer are discussed in the second paper of this series [Smith and MacInnes, THIS JOURNAL, **46**, 1398 (1924)].

that the "transference numbers," both from the ratio and from the movements of the separate boundaries, change with the concentrations of the indicator solutions. However, there is a range of concentrations of these solutions in which the value obtained from the ratio (*0.490*, for the positive ion) is equal to the value for the same ion computed from Equation 1, and also, the numbers found from the movements of the positive and negative ion add up to unity. These values are given in italics in the table. Since in these experiments the indicator concentrations were, in general, increased and decreased together, the ratio gives the correct value of the transference number throughout a wider range of concentration than do the separate boundaries. This is due to the fact that the increase or decrease of rate of movement when the indicator concentration is changed is in the same direction for both boundaries, tending to keep the ratio constant, whereas the values of the transference numbers obtained from the movement of the separate boundaries are found to vary in the same range. For careful work it does not appear to be safe to rely on the ratio alone to give the correct transference number, since, unless the indicator solutions are known to have the right concentrations, it may give results that are considerably in error. If, however, as in the case given above, the ratio and the movements of the two boundaries lead to the same value of the transference number, the worker can feel confident that the correct value has been obtained.

## Summary

A convenient apparatus for the measurement of transference numbers by the method of moving boundaries is described.

The transference numbers obtained from the ratio $T_K = V_K/(V_K + V_{Cl})$, in which $V_K$ and $V_{Cl}$ are the volumes swept through by the boundaries in which the potassium and chloride ions, respectively, are leading, have been shown to agree, for 0.1 $N$ and 0.2 $N$ potassium chloride at 25°, with values computed from the rates of movement of the separate boundaries. Transference numbers determined by the latter method involve measurements of current and time whereas values obtained from the ratio are independent of these measurements.

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## The Activities of Strong Electrolytes

## III. The Use of the Flowing Junction to Study the Liquid-Junction Potential between Dilute Hydrochloric Acid and Saturated Potassium Chloride Solutions; and the Revision of Some Single-Electrode Potentials.

by

George Scatchard

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[Contribution from the Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology, No. 167]

# THE ACTIVITIES OF STRONG ELECTROLYTES. III. THE USE OF THE FLOWING JUNCTION TO STUDY THE LIQUID-JUNCTION POTENTIAL BETWEEN DILUTE HYDROCHLORIC ACID AND SATURATED POTASSIUM CHLORIDE SOLUTIONS; AND THE REVISION OF SOME SINGLE-ELECTRODE POTENTIALS

By George Scatchard[1]

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## Introduction

One of the outstanding problems in the theory of electrolytic solutions is the determination of the activity of individual ions, in particular that of the hydrogen ion. Individual ion activities have usually been calculated through one of the three following assumptions: (a) that, for a uni-univalent electrolyte, the activities of the two ions are equal; (b) that Assumption (a) holds in the particular case of potassium chloride, and that the activity of any ion depends only upon the total molality (or ionic strength) and not upon the ions with which it is associated; (c) that the saturated potassium chloride bridge eliminates liquid-junction potentials. Practically it is unnecessary that the potential be zero if only it is the same for the reference and unknown solutions.

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[1] National Research Fellow.

Assumption (a) follows from the simple Arrhenius theory, which assumes that the ions, in so far as they exist as such, are perfect solutes. Assumption (b) was first made by MacInnes.[2] The assumption of equal activities for the potassium and chloride ions rests on their similarity in mass, mobility and atomic structure; the assumption of an individual activity independent of the other ions follows, though not as a necessary conclusion, from the consideration of the ions as distinct entities. Assumption (c) would follow from Planck's theory of liquid-junction potentials if the conductivity of the potassium chloride solution were infinitely large compared to that of the other solution, and the mobilities of potassium and chloride ions were exactly equal.[3] The general acceptance of this assumption is based largely upon the experimental work of Fales and Vosburgh.[4]

Assumptions (a) and (b) are in general incompatible. But the bases of Assumption (c) are entirely distinct from those of the other two, and it is possible to compare it with the others experimentally. Such a comparison from the existing experimental data has been given in an earlier paper.[5] The present paper describes a more detailed and accurate comparison.

To obtain the desired accuracy it seemed necessary to use the flowing junction,[6,7] which cannot be used directly with a hydrogen electrode since the change in the pressure due to the changing liquid level affects the potential at the hydrogen electrode, and since the junction is disturbed by the rocking or gas bubbling at the hydrogen electrode. Therefore the two cells, $\mathrm{Pt,H_2} \mid \mathrm{HCl,AgCl} \mid \mathrm{Ag}$ and $\mathrm{Hg} \mid \mathrm{HgCl,KCl(sat.)} \parallel$[8] $\mathrm{HCl,AgCl} \mid \mathrm{Ag}$, were used. The first, the data for which are given in the first paper of this series,[9] gives the mean activity of the hydrogen and chloride ions; the second gives the activity of the chloride ion if we assume that the liquid-junction potential is constant; with the same assumption the difference between the two gives the activity of the hydrogen ion. This method has the further advantage that, in the use of Assumption (b), it is the activity of the chloride ion which is directly measured as the mean activity of the ions of potassium chloride. Some supplementary measurements were also made of the saturated calomel electrode against silver chloride electrodes in 0.1 *N* potassium chloride.

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[2] MacInnes, This Journal, **41**, 1086 (1919).

[3] Bjerrum, *Z. physik. Chem.*, **53**, 428 (1905).

[4] Fales and Vosburgh, This Journal, **40**, 1291 (1918). See, however, Ref. 5.

[5] Scatchard, *ibid.*, **45**, 1716 (1923).

[6] Lamb and Larson, *ibid.*, **42**, 229 (1920).

[7] MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

[8] The sign $\parallel$ is here used to signify a flowing junction.

[9] Scatchard, This Journal, **47**, 641 (1925).

## Apparatus and Materials

It was necessary to make some changes in the flowing-junction apparatus of MacInnes and Yeh[7] for use with solutions of widely different densities, in order that the rate of flow of the two solutions might be approximately equal. This was accomplished by replacing the conical reservoirs with cylindrical ones, which were graduated in millimeters above the level of the liquid junction to facilitate regulating the heights of the liquid columns to inverse proportionality to the densities (which gives equal weight to the two columns). This apparatus has the further advantages that almost all of the liquid is always in the thermostat, and that the elimination of stopcocks simplifies the washing and drying. Since two liquids of unequal densities mix turbulently as soon as they turn to the vertical, the horizontal section of the outlet tube was lengthened so that the resistance of a longer column of liquid might lessen any disturbing effect of the turbulent mixing. No disturbance from this effect was noticed in the experiments.

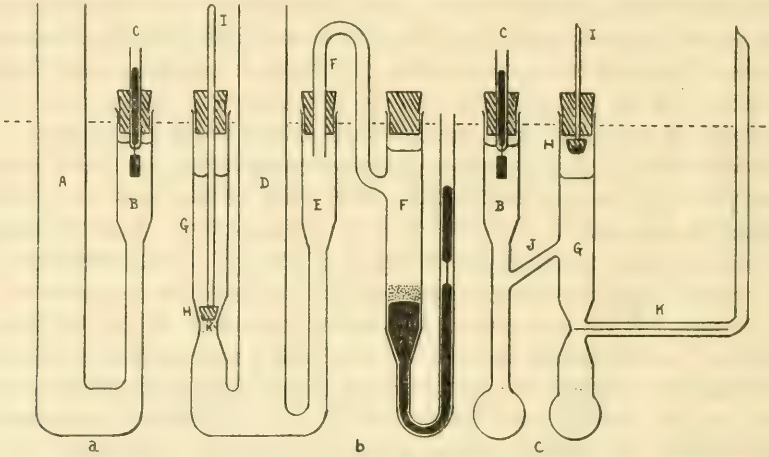

Fig. 1.

The apparatus is shown in Fig. 1, whose scale is 1:4; a represents the acid side with reservoir A, electrode vessel B, and electrode C; b is the potassium chloride side, with D the reservoir and E the tube connecting to the siphon of the calomel electrode vessel F, which is a simple form but with adequate precautions against the calomel coming into contact with the platinum wire. The liquid junction is made at the junction of tubes G and K. The two solutions are kept separated during the filling of the apparatus by the stopper H, which is later raised to the top of the apparatus by the glass rod I. In c is shown the joining of the two parts through the tube J which connects B and G. The liquid junction persists throughout the horizontal part of tube K.

The top of this tube is connected with a glass siphon, not shown in the figure, which leads outside the bath and which includes a glass stopcock and a pinchcock to regulate the rate of flow. The thermostat and potentiometer set-up were the same as those described in the previous paper.[9]

The operation of this apparatus was entirely satisfactory. Even with molal hydrochloric acid the electromotive force was constant and reproducible within a few hundredths of a millivolt.

The hydrochloric acid solutions were the same as those used in the first article of this series.[9] The potassium chloride for the salt bridge was Kahlbaum's c. p. material, recrystallized once from distilled water. For use in the electrode vessels this was further crystallized twice from distilled water. The mercury was purified by passing eight or ten times in a fine spray through a 1.5-meter column containing a dil. nitric acid solution of mercurous nitrate and was then distilled twice in a current of air under reduced pressure.[10] The calomel was prepared electrolytically from this mercury and molar hydrochloric acid,[11] and the resulting mercury-calomel paste was shaken several times with fresh portions of a saturated solution of potassium chloride. A solution saturated with both calomel and potassium chloride was prepared by long agitation of the purified paste with a saturated solution of potassium chloride.

The silver chloride electrodes were taken from the batches described in the former paper[9] and their value was corrected to the average of the batch as there described. Those used in the potassium chloride solutions were treated in the same way. Two saturated calomel electrodes were used. Their electromotive force never differed by more than 0.1 mv. and generally agreed to 0.05 mv. All values were corrected to their average.

## Measurements and Results

It is essential that the two solutions should not mix before the junction is formed. The stopper H is moistened with the acid solution before being put in place. As the potassium chloride solution is poured in, it leaves a bubble of air below this stopper, and so does not come into contact with it. At the start the exit tube is entirely filled with this solution. The acid solution is allowed to enter the tube G, by loosening the stopper at the top for a sufficient time, only when the pressure on the two sides is nearly equalized.

The stock solution of saturated potassium chloride is kept in contact with the solid salt in the thermostat. To ensure saturation, a stick of fused potassium chloride, 6 cm. long and with cross section about half as great as that of the tube, stands in the bottom of reservoir D. This stick is made by pouring the molten salt into a quartz combustion boat. The cotton thread used to remove this stick from the aqueous solution soon becomes covered with potassium chloride crystals and aids in maintaining saturation. This precaution is particularly necessary with the more concentrated acid solutions, with which a slight difference in the concentration of potassium chloride makes an appreciable difference in the potential. In the reservoir A is placed a counter-volume of glass weighted with mercury which has the same length and cross section as the salt stick.

[10] Hulett, *Z. physik. Chem.*, **33,** 611 (1900).

[11] Ellis, THIS JOURNAL, **38,** 740 (1916).

After the apparatus has been filled and left in the thermostat for 30 minutes to attain the temperature of 25°, the stopper H is raised entirely out of the liquid. The flow is started immediately. After a few seconds of rapid flow to eliminate the liquid turbulently mixed by the withdrawal of the stopper, the flow is adjusted to 3 to 7 drops per minute. The electromotive force of the cell is then read every five minutes. After it has become constant within a few hundredths of a millivolt for half an hour the flow is stopped for one to three hours to study the behavior on stopping. During this time the electromotive force changes about three millivolts. Then the flow is started again and readings taken every five minutes until the value becomes constant once more. Then a second study is made of the effect of stopping the flow. On the second day the whole procedure is repeated.

This gives for each solution four measurements of the electromotive force with flowing junction and four determinations of the effect of stopping the flow. In Table I is given in the first column the molality of the solution, in the second the average of the four readings, and in the third column the mean deviation of the individual values from this average. In those cases in which the number of determinations was other than four, the number follows the third column in parenthesis. All values are in millivolts. The agreement between the different measurements on a single solution is very good. The two cases in which the mean deviation is as great as 0.1 mv. are early determinations made before the method of keeping the potassium chloride solution saturated was perfected.

Table I

Electromotive Force in Millivolts of Cells Hg | HgCl, KCl(sat.) || HCl, AgCl | Ag

| Molality of acid | $E$ | Deviation from average | $E_0'$ | Deviation from curve |
|---|---|---|---|---|
| 0.01000 | +97.83 | 0.03 | −20.47 | −0.39 |
| .01002 | 98.01 | .07 | 20.22 | − .14 |
| .01010 | 97.50 | .04 | 20.55 | − .58 |
| .01031 | 96.86 | .02 (3) | 20.66 | − .94 |
| .04986 | 59.65 | .03 | 17.37 | + .01 |
| .05005 | 59.54 | .03 (3) | 17.39 | − .01 |
| .09642 | 44.21 | .01 | 15.87 | + .02 |
| .09772 | 43.87 | .10 | 15.87 | ± .00 |
| .09834 | 43.78 | .. (1) | 15.80 | + .05 |
| .2030 | 26.69 | .00 | 14.27 | − .02 |
| .3063 | 16.75 | .01 (2) | 13.65 | + .01 |
| .3981 | 10.18 | .03 | 13.48 | + .03 |
| .5009 | 3.99 | .05 | 13.77 | − .15 |
| .5013 | 4.09 | .02 | 13.65 | − .03 |
| .6367 | − 2.37 | .01 | 13.97 | + .06 |
| .9377 | −13.93 | .01 | 15.59 | ± .00 |
| 1.0008 | −16.02 | .02 | 16.00 | ± .00 |
| 1.5346 | −31.00 | .13 (5) | 20.00 | ± .00 |

The data were treated as were those on cells without transference in the previous paper[9] except that the numerical coefficients are taken half as large for the single electrode. $E_0'$ was calculated from the equation $E_0' = E + 59.15 \log m$, where $E$ is the electromotive force of the cell and $m$ the molality. The values of $E_0'$ are given in the fourth column of Table I. These values were plotted against $\sqrt{m}$ and a smooth curve drawn through them which approached asymptotically the line with slope $29.575\ \sqrt{m}$. Values taken from this curve at rounded molalities were tested to see if the deviation from the linear asymptote was proportional to $m$, and the extrapolated value at zero concentration was shifted until such proportionality was attained. The final curve is fitted by the equation $E_0' - E_0 = 29.575\sqrt{m} - Bm$, ($B = 23.6$) through a wider range than any of the curves for the cells without transference. The value of $E_0$, the extrapolated value of $E_0'$ at zero concentration, is —22.80 millivolts.

The deviations of the individual points from this curve are given in the fifth column of Table I. The agreement is very good except at 0.01 $M$, and there the deviation of the individual points is not larger than might be expected from the differences between the various determinations. The direction of the deviation is the same as for other electromotive-force determinations in dilute solutions. Probably these solutions are too dilute for accurate measurements with the technique used in this work.

TABLE II

ACTIVITY COEFFICIENTS OF THE IONS OF HYDROCHLORIC ACID

| Molality | $\gamma_{Cl^-}$ F. J. | $\gamma_{Cl^-}$ MacInnes | $\gamma\sqrt{H^+ \times Cl^-}$ | $\gamma_{H^+}$ F. J. | $\gamma_{H^+}$ MacInnes |
|---|---|---|---|---|---|
| 0.001 | 0.965 | 0.965 | 0.966 | 0.967 | 0.967 |
| .002 | .952 | .951 | .954 | .956 | .956 |
| .005 | .926 | .926 | .932 | .937 | .937 |
| .01 | .899 | .899 | .910 | .921 | .921 |
| .02 | .866 | .865 | .881 | .887 | .888 |
| .05 | .809 | .809 | .836 | .863 | .863 |
| .1 | .762 | .762 | .801 | .841 | .842 |
| .2 | .718 | .715 | .774 | .834 | .838 |
| .3 | .701 | .688 | .763 | .829 | .845 |
| .4 | .696 | .669 | .760 | .829 | .863 |
| .5 | .700 | .654 | .763 | .833 | .890 |
| .6 | .707 | .642 | .770 | .838 | .923 |
| .75 | .725 | .627 | .783 | .845 | .978 |
| 1.0 | .767 | .605 | .817 | .871 | 1.103 |

The values for the activity coefficient of the chloride ion, assuming that the liquid-junction potential is constant with the flowing junction ($\gamma_{Cl^-}$, F. J.), are calculated from the equation $E_0 - E_0' = 59.15 \log \gamma$. They are given for rounded molalities in the second column of Table II. The third column contains the mean activity coefficient of the ions of potassium chloride, which is equal to the activity coefficient of the chloride ion in hydrochloric acid ($\gamma_{Cl^-}$, MacInnes) according to assumption (b)—that the activities of the chloride and potassium ions are equal and also independent of the ions with which they are associated. The fourth column gives the mean activity coefficient of the hydrogen and chloride ions ($\gamma_{\sqrt{H^+ \times Cl^-}}$), which is also the activity coefficient of the chloride or hydrogen ion according to Assumption (a)—that the two activities are equal. The fifth and sixth columns give the activity coefficients of the hydrogen ion according to Assumptions (c) and (b). These values are obtained by dividing the square of the quantity in the fourth column by the quantity in the second and third columns, respectively. The logarithms of these activity coefficients are plotted against $\sqrt{m}$ in Fig. 2.

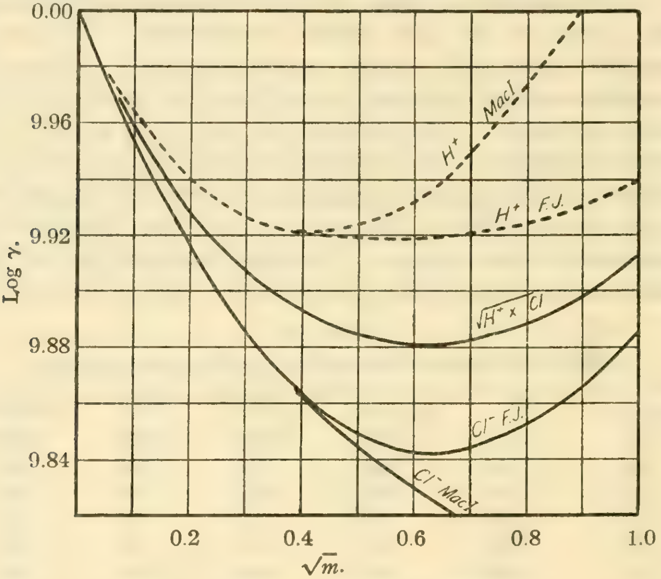

Fig. 2.—Log $\gamma$. Hydrochloric acid.

The comparison of these assumptions may be made more clear by determining the electromotive force which must exist at the liquid junction if either of the first two assumptions is true. The values of this potential are plotted against the molality in Fig. 3. The liquid-junction potential is arbitrarily taken as zero when the molality is zero, without assuming, however, that its value actually is zero. The upper curve refers to Assumption (a) and the corresponding ordinates are given on the right side. The lower curve, whose ordinates are given on the left, refers to Assumption (b).

It is highly probable that liquid-junction potentials are due to the different mobilities of the ions. Since the hydrogen ion has a greater mobility than the chloride ion, there should be a potential increasing with the concentration and negative as the cell is written. This is fulfilled by the curve representing the MacInnes assumptions. On the other hand, the curve for the liquid-junction potential assuming equal activities for the hydrogen and chloride ions passes through a minimum. In the more dilute solutions the change with changing acid concentration is in the opposite direction to that predicted from the mobilities of the ions. This alone appears to me to be sufficient evidence to disprove the hypothesis that the ions of hydrochloric acid have equal activities.

If the liquid-junction potential is due to mobility differences, and therefore must be negative as represented in Fig. 3, the values of $\gamma_{\text{Cl}^-}$, F. J. given in Table II must be maximum values. Those of $\gamma_{\text{Cl}^-}$, MacInnes are, on the other hand, minimum values unless the activity of the chloride ion is less than that of the potassium ion. For the more concentrated solutions, where there is a considerable difference between the two values, indirect evidence points to values of the activity of the chloride ion much nearer to the minimum than to the maximum, but the evidence is not very conclusive. At 0.2 *M* the difference between the two values is only 0.3% which corresponds to 0.1 mv. or about the experimental error; up to 0.1 *M* the two are identical. In the very dilute solutions this identity may be ascribed to the method of extrapolation but the experimental results themselves are entirely concordant at 0.05 and 0.1 *M*. Even at 0.01 *M* the agreement between the experimental measurements by the two methods is much better than the agreement of either with the smoothed curve.

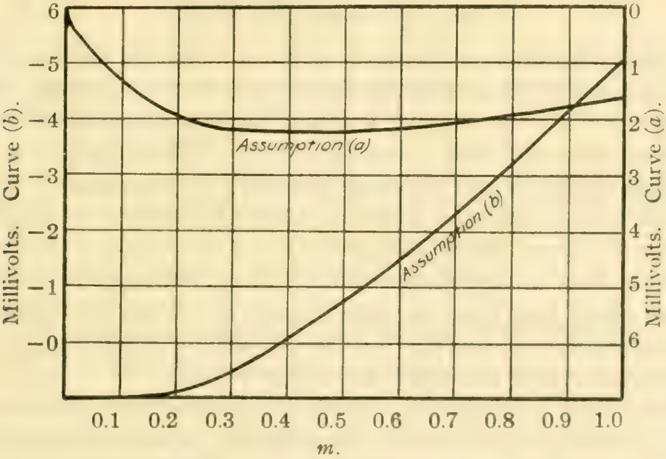

Fig. 3.—Liquid-junction potentials.

Brönsted[12] has shown that the assumption that the activity of the choride ion is the same in solutions of hydrochloric acid and of potassium chloride of the same molality is contrary to the laws of thermodynamics, since the activity of water in the two solutions is different. His argument gives no indication of the magnitude of the difference demanded by thermodynamics. The results of the present paper give evidence that it is so small up to 0.1 $M$ that the activity of the chloride ion is given to a few tenths of a per cent. by either the MacInnes assumptions or the assumption that the saturated potassium chloride bridge with a flowing junction gives a liquid-junction potential independent of the acid concentration. The agreement between these two methods is even more striking when it is recalled that, not only do they give the maximum and probable minimum values, respectively, but the assumptions upon which they are based are independent and of entirely different natures. The fact that they lead to the same results gives strong support to each.

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[12] Private communication to Lewis and Randall. See their [illegible] "Thermodynamics," McGraw-Hill Book Co., 1923, p. 368.

### Effect of Stopping the Flow

The flowing junction presumably gives a "mixture boundary,"—one in which the composition of each infinitesimal layer is the same as though it had been prepared by stirring together the two solutions in the proper proportions, and one which is extremely thin. When the flow is stopped the junction changes to a "diffusion boundary,"—one whose composition is determined by the rates of diffusion of the various ions, which gradually increases in thickness. Any change in the total electromotive force of the cell when the flow is stopped must be due to the difference between the potentials of these two types of liquid junction. Then the effect on the electromotive force of stopping the flow should give some insight into the absolute magnitude of the liquid-junction potential.

When the flow is stopped the total electromotive force becomes more positive, indicating a decrease in the negative liquid-junction potential, at first rapidly and then more slowly. For 0.2 $M$ and more concentrated solutions it reaches a maximum in about two hours and then decreases almost linearly. The maximum change is about 3.5 millivolts. The 0.05 and 0.1 $M$ solutions reach the same maximum but remain constant. The 0.01 $M$ solution increases slowly for at least six hours. For a solution of any given concentration the change in any given time is reproducible within a few hundredths of a millivolt. The fact that the electromotive force returns to the original value when the flow is started again proves that all the change is in the liquid junction potential. In Fig. 4 is plotted the change with time of the electromotive force of 0.01, 0.1 and 1.0 $M$ solutions, which are typical of the three classes. Each curve is a slightly smoothed composite of four determinations.

These measurements show that, for some unknown reason, the potential drop at a diffusion boundary is independent of the thickness of that boundary in 0.05 and 0.1 $M$ solutions. Also, since there is a difference of about

3.5 mv. between the liquid-junction potentials at a "mixture boundary" and at a "diffusion boundary," both cannot be zero and it is probable that neither is. Since this difference is almost independent of the acid concentration, it appears that at least the order of magnitude of the potential must be the same in dilute as in concentrated solutions.

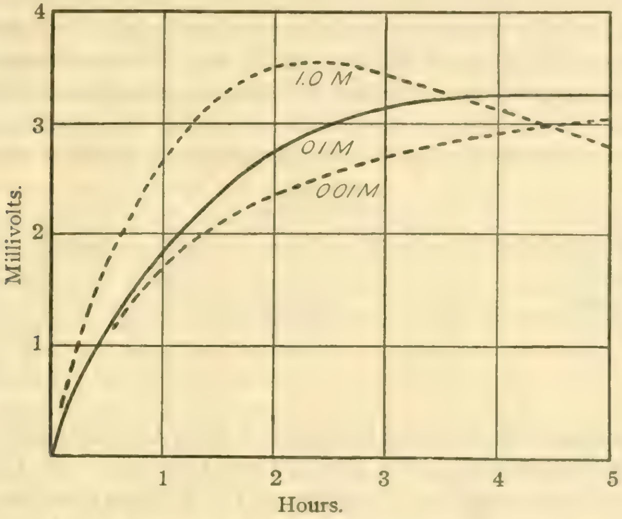

Fig. 4.—Effect of stopping flow.

## The Absolute Value of the Liquid-Junction Potential

Using the MacInnes assumptions, it is possible to determine the absolute magnitude of this liquid-junction potential. If the activity of the chloride ion is the same in the two solutions, the only difference in electromotive force between the two cells Hg | HgCl,KCl(sat.) || HCl($c_1$),AgCl | Ag and Hg | HgCl,KCl(sat.) || KCl($c_1$),AgCl | Ag is in the liquid junction. If the activities of the potassium and chloride ions are equal, the liquid-junction potential between two solutions of potassium chloride is given by the equation, $E_b = \int (0.5 - t_+) \mathrm{d} E = 59.15 \int (0.5 - t_+) \mathrm{d} \log a_\pm$, where $E_b$ is the liquid-junction potential, $E$ is the electromotive force of the concentration cell without transference, $t_+$ is the transference number of the potassium ion, and $a_\pm$ is the mean activity of the ions.

For the graphic integration of this last equation, the activity of the ions of potassium chloride at 20°, determined from vapor-pressure measurements,[9] was used. The values of $t_+$ were determined from the equation $1 - 2t_+ = 0.005 + 0.028\sqrt{m}$, which fits the experimental determinations at 0.01, 0.1 and 1.25 *M*. The value of $E_b$ between 0.1 *M* and saturated (4.1 *M*) potassium chloride is 2.7 mv. This involves a large extrapolation of the transference number, but even if $t_+$ is assumed to be constant in solutions more concentrated than 1.25 *M* the value is reduced only to 2.4 mv. The greatest uncertainty probably lies in the extension of the assumption of equal activities even to the saturated solution. The final result may be in error as much as 1 mv., but it does give an approximate value for the liquid-junction potential.

To determine the difference in liquid-junction potential with potassium chloride and with hydrochloric acid three measurements were made on the cell, Hg | HgCl,KCl(sat.) || KCl($c_1$),AgCl | Ag. The results are given in Table III. As predicted from the fact that the electromotive force of a concentration cell is independent of the nature of the junction, the electromotive force of these cells was unchanged when the flow was stopped.

Table III

Electromotive Force of Cell Hg | HgCl, KCl (sat.) || KCl ($c_1$), AgCl | Ag

| Molality | $E$ | $E_0'$ | $E_0'_{\text{HCl}}$ | Difference |
|---|---|---|---|---|
| 0.09040 | 47.52 | −14.22 | −16.04 | 1.82 |
| .10006 | 45.40 | 13.73 | 15.80 | 2.07 |
| .10057 | 45.23 | 13.77 | 15.79 | 2.02 |
| | | | Av. | 1.97 |

The liquid-junction potential between 0.1 *M* hydrochloric acid and saturated potassium chloride is the sum of these two values, or 4.7 mv., the acid solution being negative. A glance at Fig. 3 shows that this potential is constant in more dilute solutions, but increases to about 11.0 mv. with molar hydrochloric acid. It must be remembered that this calculation of the liquid-junction potential depends upon the acceptance of the MacInnes assumptions as exact even in concentrated solutions.

## Some Single-Electrode Potentials

The experiments and calculations of this and the previous paper permit the calculation of some single-electrode potentials at 25° more accurately than has previously been possible. I shall follow Lewis and Randall[13] in arbitrarily fixing as zero the potential difference between hydrogen at atmospheric (partial) pressure and hydrogen ion with an activity of one, and also in their use of symbols.

**Ag | AgCl(s), Cl⁻.**—The e.m.f. of this electrode is given directly by —$E_0$ for the cell, Pt,$H_2$ | HCl,AgCl | Ag. Although Lewis and Randall find —0.2234 volt by this method, they prefer the value —0.2245 determined from their value for the calomel electrode and the difference between calomel and silver chloride electrodes. Since the measurements of Linhart permit an extrapolation for this cell more accurate than for any other, it is more reasonable to accept the direct determination of this e.m.f. and to determine that for the calomel electrode from the difference.

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[13] Ref. 12 a. Chap. XXX.

Taking the more accurate extrapolation of my previous paper, we have: *Ag | AgCl(s),Cl⁻. $E^0$ = —0.2226 volt.*[14]

**Hg | HgCl(s), Cl⁻.**—The cell Pt, $H_2$ | HCl(0.1 *M*), HgCl | Hg has been measured by many observers with the following results: 0.3991,[15] 0.3988,[16] 0.3988,[17] and 0.3989;[18] av., 0.3989. Using 0.0814 for the mean activity of hydrogen and chloride ions in 0.1 *M* hydrochloric acid, Lewis and Randall find —0.2700 volt for $E^0$ of the calomel electrode. Taking from my previous paper 0.0801 as the mean activity, we obtain *Hg | HgCl(s),Cl⁻. $E^0$ = —0.2692 volt.* This corresponds to a difference of 0.0466 volt between the calomel and silver chloride electrodes.

**Saturated Calomel Electrode (S. E.), Flowing Junction.**—The e.m.f. of this electrode is given by the difference in $E_0$ for the cells, Pt,$H_2$ | HCl,-AgCl | Ag and Hg | HgCl,KCl(sat.) || HCl,AgCl | Ag. It must be remembered that this derivation assumes that the flowing junction is between the saturated potassium chloride and 0.1 *M* or more dilute hydrochloric acid. The value would probably be approximately the same for any other electrolyte in concentration not greater than 0.1 *M*. *S. E., Flowing Junction. E = —0.2454 volt.*

**Tenth-Molal Calomel Electrode (D. E.) | KCl(sat.), Flowing Junction.**—Combining the value for the last electrode with 0.0453 volt, from Table III for the cell Hg | HgCl,KCl(sat.) | KCl(0.1 *M*),AgCl | Ag, and 0.0466 volt for the difference between these silver chloride electrodes and calomel electrodes, we have *D. E. | KCl(sat.), Flowing Junction. E = —0.3373 volt.*[19] This is in fair agreement with the value —0.3376 volt given by Sörensen[20] and generally accepted for hydrogen-ion determinations using the saturated potassium chloride bridge.

**D. E. (0.1 *M* Calomel Electrode without Liquid-Junction Potential).**—Lewis and Randall calculate the e.m.f. of this electrode from $E^0$ for Hg | HgCl(s),Cl⁻ and from the activity of 0.1 *M* potassium chloride and with their values for these two they obtain —0.3351 volt. The calculation assumes that the activities of potassium ion and chloride ion are equal. Sörensen's value for the 0.1 *N* electrode,[19] corrected by using 0.0801 instead of 0.0917 for the mean activity of the ions of 0.1 *M* hydrochloric acid, becomes —0.3342 volt. Using my value for $E^0$, and taking 0.0762 for the activity of the chloride ion in 0.1 *M* potassium chloride,[9] we have *D. E.* $E = -0.3353$ *volt.* The differences between the values used for various quantities by Lewis and Randall and by myself have nearly canceled out in the calculation of the e.m.f. of this electrode.

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[14] This value holds for the silver chloride electrodes prepared by three different methods by Linhart, by Noyes and Ellis and by me. Gerke [THIS JOURNAL, 44, 1684 (1922)] found 0.0455 volt for the difference between his silver chloride and calomel electrodes, which gives —0.2237 for $E^0$ for his silver chloride electrodes.

[15] Harned, THIS JOURNAL, **37**, 2475 (1915).

[16] Ellis, *ibid.*, **38**, 752 (1916).

[17] Loomis and Meacham, *ibid.*, **38**, 2315 (1916).

[18] Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917).

[19] 0.1 *N* Potassium chloride is 0.1006 *M*, so the value (negative) of the 0.1 *N* electrode is 0.00015 volt less than that of the 0.1 *M* electrode.

[20] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., 1923, Chap. XIX.

A comparison of the last two electrode potentials gives 2.0 mv. as the difference between the liquid-junction potentials of saturated potassium chloride with 0.1 *M* potassium chloride and with 0.1 *M* hydrochloric acid, which is identical with the value determined in the last section. The determination in this section involves the extrapolation of the activity coefficients of both hydrochloric acid and potassium chloride and the assumption that the activity of the potassium ion equals that of the chloride ion. The previous determination involves only the assumption that the activity of the chloride ion is the same in 0.1 *M* hydrochloric acid as in 0.1 *M* potassium chloride. Although there is, of course, some possibility of compensating errors, the agreement between these two results is considered a valuable confirmation of the accuracy of the activity determinations, and of the assumptions of MacInnes applied to 0.1 *M* solutions.

In conclusion I wish to express my gratitude to the National Research Council for its financial assistance, and to Professor F. G. Keyes and the other members of the staff of this Laboratory, especially to Professor D. A. MacInnes, for the suggestions and help they have given.

## Summary

1. Using a flowing-junction apparatus which gives results constant and reproducible within a few hundredths of a millivolt, the electromotive force at 25° of the cell, $Hg \mid HgCl, KCl(sat.) \parallel HCl(c_1), AgCl \mid Ag$, has been measured with acid concentration varying from 0.01 to 1.5 *M*.

2. On stopping the flow the liquid-junction potential changes about 3.5 mv. The exact behavior depends upon the acid concentration.

3. For 0.1 *M* solutions and those more dilute, the results give striking confirmation of the conclusion that the saturated potassium chloride bridge gives a liquid-junction potential that does not vary with the acid concentration, and of the assumptions of MacInnes regarding individual ion activities.

4. For more concentrated solutions the results give a maximum value for the activity of the chloride ion, and a minimum value for the activity of the hydrogen ion.

5. Making the MacInnes assumptions, the liquid-junction potential, with flowing junction, between saturated potassium chloride and dilute hydrochloric acid is calculated as 4.7 mv.

6. From the data of this paper and of the first two of this series, the following are determined as the most probable values for some single electrode potentials at 25°: $Ag \mid AgCl(s), Cl^-$, —0.2222 volt; $Hg \mid HgCl(s)$,

$Cl^-$, —0.2692 volt; S. E., flowing junction, —0.2454 volt; D. E. | KCl(sat.), flowing junction, —0.3373 volt; D. E. (without liquid-junction potential), —0.3353 volt.

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# THE DENSITIES, EQUIVALENT CONDUCTANCES AND RELATIVE VISCOSITIES AT 25°, OF SOLUTIONS OF HYDROCHLORIC ACID, POTASSIUM CHLORIDE AND SODIUM CHLORIDE, AND OF THEIR BINARY AND TERNARY MIXTURES OF CONSTANT CHLORIDE-ION-CONSTITUENT CONTENT

by

Charles E. Ruby and Juntaro Kawai

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# THE DENSITIES, EQUIVALENT CONDUCTANCES AND RELATIVE VISCOSITIES AT 25°, OF SOLUTIONS OF HYDROCHLORIC ACID, POTASSIUM CHLORIDE AND SODIUM CHLORIDE, AND OF THEIR BINARY AND TERNARY MIXTURES OF CONSTANT CHLORIDE-ION-CONSTITUENT CONTENT

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The object of this investigation was to make a systematic study, over a wide range of concentration, of the conductances of solutions of pairs of uni-univalent electrolytes, having a common-ion constituent, with the hope of disclosing the nature of such solutions, and to test the value of the methods of calculating the conductances of solutions of such mixtures of electrolytes, that have been proposed by earlier workers in this field.

According to the original theory of electrolytic dissociation, the ratio of the equivalent conductance of a solution at any concentration to its equivalent conductance at infinite dilution is a measure of the degree of dissociation of the electrolyte present, provided that the viscosity of the solution does not differ appreciably from that of pure water. In solutions of greater viscosities, the frictional resistance to the motion of the ions may be appreciably different from that in very dilute solutions. The conductance ratio, therefore, cannot be an exact measure of the ionization. Later, with the assumption that the mobilities of the separate ions vary inversely with the viscosity, the conclusion was reached that the product of the measured equivalent conductance and the relative viscosity of a solution of an electrolyte to its equivalent conductance at infinite dilution afforded a truer measure of its degree of dissociation in that solution.

As a means of computing the concentration of ions present in a given solution, the conductance-viscosity ratio has lost much of its value. Researches in recent years have shown that the concentration-ionization product is not a measure of the quantity of ions present, in the sense of the ordinary mass-action law. But the property of viscosity is quite intimately related to the conduction of electricity by solutions of electrolytes, for such conduction is accompanied by transference of matter through the solutions. Therefore, a supplemental study of the relative viscosities of a number of solutions was made, with the desire of correlating, if possible, these two properties.

In all previous conductivity work, with the exception of that of Stearn,[1] the concentrations have been computed upon a volume basis. In certain respects it is more advantageous to employ the weight molal basis of reckoning concentration, that is, moles per thousand grams of water. In the present paper this method has been employed. For the computation of the equivalent conductances, accurate density measurements were required. These measurements were made with a pycnometer. With these density data the conductance and relative viscosity measurements of this investigation were compared with measurements of other investigators who employed volume concentrations, and were found to be in moderately satisfactory concordance.

The electrolytes chosen for study were hydrochloric acid, potassium chloride and sodium chloride, which show wide differences in the properties under investigation but which are typical uni-univalent electrolytes, having an ion constituent in common. In addition to the investigation of the three properties of solutions of electrolytes and of their binary mixtures, a similar study of their ternary mixtures was made.

The electrical conductances of solutions of hydrochloric acid, potassium chloride and sodium chloride, varying in concentrations from 0.0001 $N$ to 1 $N$ have been thoroughly studied,[2] but relatively little work has been done upon mixtures of solutions of these electrolytes. In 1911 Bray and Hunt[3] made measurements of the conductances of solutions of sodium chloride and hydrochloric acid at 25° (in none of which the total electrolyte concentration exceeded 0.2 mole per liter).

Stearn has made a study of the equivalent conductances, densities and relative viscosities of solutions of some of the alkali halides and of their mixtures. He employed weight concentrations in his work and his selection of the concentrations studied coincides to some extent with that employed in this work.[4] Where comparison is possible, that is, in the cases of the potassium and sodium chloride solutions and their mixtures, the agreement between the electrical conductance data given in his paper and those in this article is not so concordant as can be expected, for the numerical differences do not lie within the limits of experimental error, but the trends of the two sets of data are identical.

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[1] Stearn, THIS JOURNAL, **44**, 670 (1922).

[2] Noyes and Falk, *ibid.*, **34**, 454 (1912).

[3] Bray and Hunt, *ibid.*, **33**, 781 (1911).

[4] The experimental work of this paper was completed before September, 1921.

Employing the assumption that the apparent equivalent conductances of the mixtures can be computed by the alligative formula from the equivalent conductances of solutions of pure salts of concentrations equal to the total salt concentrations of the mixture, he compared his observed figures with these calculated values. In almost all cases he found that the calculated values were the larger, and that the differences increased with increasing total salt concentration. He suggested that these results could be explained upon the basis of complex formation, but no quantitative computations involving the formation of complex ions were offered.

The most precise data on the densities of potassium and sodium chloride solutions are those of Baxter and Wallace[5] whose results at 25° when recalculated to a weight molal basis were found to be in close agreement with the measurements of this paper. Equally accurate measurements on hydrochloric acid are not available. With the exception of the figures of Stearn, density measurements upon solutions of mixed electrolytes made in a systematic manner are not available.

There are at present no accurate measurements on the relative viscosities of the solutions studied in this investigation, since even the work of Stearn on this property of mixed electrolytes must be regarded as only approximate.

## Preparation of the Solutions

The hydrochloric acid was purified by the method of Hulett and Bonner.[6] The exact strength of the stock solution thus produced was determined in the usual manner by precipitation and weighing of silver chloride.

The solutions, hereinafter termed "primary solutions," of each of the electrolytes were prepared by combining appropriate weights of the stock solutions of hydrochloric acid, and of the crystals of potassium and sodium chlorides with the calculated quantities of distilled water, in order to produce the desired concentrations. All weights were reduced to vacuum.

Seven concentrations of the primary solutions were studied, namely, 0.1, 0.2, 0.5, 1, 2, 3 and 4 weight normal.

The binary mixtures of the three pairs of electrolytes were made by mixing appropriate weights of the primary solutions, so that the mole-per cent. ratios of the two electrolytes were 20:80, 40:60, 60:40, 80:20.

For each of the total concentrations of 1, 2 and 4 weight normal, twelve binary mixtures were studied, while for the lower concentrations fewer binary mixtures were examined, because it became apparent that for concentrations less than 0.5 weight normal, all of the properties investigated became practically linear.

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[5] Baxter and Wallace, This Journal, **38**, 70 (1916).

[6] Hulett and Bonner, *ibid.*, **31**, 390 (1909).

The ternary mixtures of the three electrolytes were prepared by mixing different amounts by weight of the three primary solutions and computing the concentration ratios. An effort was made to approximate to the ratios 20:20:60, 20:40:40, 20:60:20, 40:20:40, 40:40:20 and 60:20:20, in mole percentages of the three electrolytes, but no attempt was made to secure these exact ratios.

For each of the total concentrations of 1, 2 and 4 weight normal, six ternary mixtures were examined; for the concentrations of less than 0.5 weight normal, no ternary mixtures were studied; for the 0.5 weight normal concentration, one ternary mixture was investigated. The values of the three properties of mixtures, whose total electrolyte concentrations are 0.1 weight normal or less, can be computed by the alligative formula.

## Methods of Procedure and Degrees of Precision Obtained

**Electrical Conductance.**—The usual conductivity apparatus, consisting of a Kohlrausch bridge, a four-dial, Curtis-coil resistance box, a constant speed, high-frequency generator, a telephone, adjustable condensers and conductivity cells, was used for making the conductance measurements. The central tenth of the bridge wire was calibrated with the help of resistances precise to one part in five thousand. The precision attainable in reading the bridge was never less than one part in two thousand. The wire leads were in all cases of negligible resistance in comparison with the resistances measured. All measurements were made at a temperature of 25° ± 0.02°, whose constancy was maintained by the use of an asbestos jacketed thermostat fitted with a stirring device, a heating coil, and a thermoregulator. Two conductivity cells were employed whose constants, 33.29 and 659.9, respectively, were determined by the aid of a solution of potassium chloride having the composition of one part of potassium chloride to 12.998 parts of water, and a specific conductance at 25° of 0.1118 mhos. The precision of the recorded conductance data is not less than one part in one thousand, and may be somewhat better.

**Densities.**—The density measurements made at 25° ± 0.02° by the use of a glass pycnometer of the Sprengel type having a volume of 18.6896 cc. are not less precise than one part in twenty-five hundred. That the solutions studied had no appreciable solvent action upon the pycnometer was shown by its substantial constancy of weight throughout this investigation.

**Relative Viscosities.**—The measurements of relative viscosities were made with an instrument of the Ostwald type, for the construction of which, as well as for the construction of the two conductivity cells great thanks are due to Professor F. G. Keyes of this Laboratory. In the designing and construction of the instrument, the precautions given by Washburn and Williams[7] were carefully observed. The viscosimeter was immersed in a constant-temperature thermostat (25° ± 0.02°) provided with a glass window, through which the times of flow could be observed.

The period of time of flow was measured with the aid of a stop watch which was compared with a standard chronometer. Readings with this instrument could be duplicated to a fifth of a second, yielding a precision of measurement of at least one part in three thousand. The precision of the recorded relative-viscosity measurements is not less than one part in two thousand.

## Discussion of the Data

**Equivalent Conductances.**—In Table I are given the measured data on the equivalent conductances, densities and viscosities of all the solutions studied, together with the conductance-relative viscosity values.

Four theories have been advanced to account for the conductances of solutions of mixtures of electrolytes.

1. The first theory regards such solutions as mixtures of simple and complex ions and un-ionized molecules. This theory cannot be discussed from the standpoint of data obtained in this investigation, as it does not readily permit quantitative examination.

2. The second theory is based upon the principle of isohydry. This theory was employed by Bray and Hunt in the treatment of their results, but its application to the data of several of the mixtures studied in this investigation has shown it to be of little value.

3. A third method to correlate these data consists in the assumption that the conductance of any mixture may be computed from the equation $\Lambda = \bar{\gamma}\bar{\Lambda}_0$. $\bar{\Lambda}_0$ is the apparent equivalent conductance of the mixture at infinite dilution, and may be computed by the equation $\bar{\Lambda}_0 = x\Lambda_0' + y\Lambda_0'' + (1-x-y)\Lambda_0'''$ in which the $\Lambda$'s with the zero subscripts are the equivalent conductances at infinite dilution of the pure electrolytes, and $x$, $y$ and $(1-x-y)$ are the mole fractions of the electrolytes present in the mixtures; $\bar{\gamma}$ is the apparent or "mean" ionization in the mixture, and may be computed from the ionizations of the pure electrolytes in solutions of the same total electrolyte concentration by the equation, $\bar{\gamma} = x\gamma' + y\gamma'' + (1-x-y)\gamma'''$, where $\gamma'$, $\gamma''$ and $\gamma'''$ are the ionizations of the pure electrolytes in solutions of the same total electrolyte concentration and $x$, $y$ and $(1-x-y)$ are the mole fractions of these electrolytes present in the mixture. The resulting expression (for the binary mixtures) $\Lambda = [\Lambda_0'\gamma'] + [(1-x)\Lambda_0''\gamma''] + [1-x][\Lambda_0''\gamma' + \Lambda_0'\gamma'']$ is a quadratic in $x$, which may yield curves convex upward or downward depending upon the values of the constants of the equation but generally convex upward,

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[7] Washburn and Williams, This Journal, 35, 737 (1913).

that is, with maxima. This equation is applicable as it stands only to series of mixtures of the type studied, since only implicitly does it contain the concentrations of the electrolytes present.

Table I

Observed Values of Equivalent Conductances, Densities, Relative Viscosities and Equivalent Conductance—Relative Viscosity Products

| Concns., moles per 1000 g. of water | | | | | | |
|---|---|---|---|---|---|---|
| HCl | KCl | NaCl | $\Lambda$ | $\delta$ | $\eta$ | $\Lambda\eta$ |
| 0.1 | 0.0 | 0.0 | 391.33 | 0.9989 | 1.0068 | 394.00 |
| .0 | .1 | .0 | 129.02 | 1.0018 | 1.0003 | 129.06 |
| .0 | .0 | .1 | 106.82 | 1.0012 | 1.0095 | 107.83 |
| .2 | .0 | .0 | 381.25 | 1.0007 | 1.0137 | 386.47 |
| .0 | .2 | .0 | 124.11 | 1.0064 | 0.9997 | 124.07 |
| .0 | .0 | .2 | 101.69 | 1.0053 | 1.0184 | 103.56 |
| .08 | .0 | .12 | 210.03 | 1.0033 | 1.0165 | 213.49 |
| .12 | .0 | .08 | 264.92 | 1.0025 | 1.0156 | 269.05 |
| .5 | .0 | .0 | 361.31 | 1.0058 | 1.0317 | 372.76 |
| .4 | .1 | .0 | 312.67 | 1.0086 | 1.0250 | 320.48 |
| .3 | .2 | .0 | 263.56 | 1.0114 | 1.0182 | 268.30 |
| .2 | .3 | .0 | 215.27 | 1.0143 | 1.0112 | 217.64 |
| .1 | .4 | .0 | 165.65 | 1.0171 | 1.0048 | 166.48 |
| .0 | .5 | .0 | 117.52 | 1.0199 | 0.9983 | 117.32 |
| .0 | .3 | .2 | 107.80 | 1.0188 | 1.0169 | 109.63 |
| .0 | .2 | .3 | 103.08 | 1.0183 | 1.0264 | 105.76 |
| .0 | .0 | .5 | 93.94 | 1.0172 | 1.0456 | 98.26 |
| .2 | .0 | .3 | 196.84 | 1.0127 | 1.0398 | 204.71 |
| .3 | .0 | .2 | 250.93 | 1.0104 | 1.0369 | 260.21 |
| .167 | .167 | .166 | 188.63 | 1.0145 | 1.0242 | 193.16 |
| 1.0 | .0 | .0 | 333.52 | 1.0143 | 1.0617 | 354.11 |
| .8 | .2 | .0 | 291.07 | 1.0198 | 1.0483 | 305.13 |
| .6 | .4 | .0 | 247.82 | 1.0253 | 1.0351 | 256.52 |
| .4 | .6 | .0 | 202.38 | 1.0308 | 1.0221 | 206.85 |
| .2 | .8 | .0 | 157.23 | 1.0362 | 1.0102 | 158.83 |
| .0 | 1.0 | .0 | 112.29 | 1.0416 | 0.9985 | 112.12 |
| .0 | 0.8 | .2 | 106.88 | 1.0405 | 1.0166 | 108.65 |
| .0 | .6 | .4 | 101.54 | 1.0395 | 1.0352 | 105.11 |
| .0 | .4 | .6 | 96.24 | 1.0384 | 1.0537 | 101.41 |
| .0 | .2 | .8 | 91.14 | 1.0374 | 1.0736 | 97.85 |
| .0 | .0 | 1.0 | 86.07 | 1.0363 | 1.0936 | 94.13 |
| .2 | .0 | .8 | 132.98 | 1.0320 | 1.0862 | 144.44 |
| .4 | .0 | .6 | 182.07 | 1.0275 | 1.0797 | 196.58 |
| .6 | .0 | .4 | 232.12 | 1.0231 | 1.0736 | 249.20 |
| .8 | .0 | .2 | 283.19 | 1.0187 | 1.0676 | 302.33 |
| .5984 | .2007 | .2009 | 237.08 | 1.0244 | 1.0538 | 249.84 |
| .4023 | .1990 | .3987 | 189.33 | 1.0286 | 1.0593 | 200.56 |
| .4013 | .3973 | .2014 | 195.91 | 1.0297 | 1.0412 | 203.98 |
| .2051 | .5920 | .2029 | 152.11 | 1.0350 | 1.0296 | 156.61 |
| .2000 | .3996 | .4004 | 145.00 | 1.0441 | 1.0471 | 151.83 |
| .2044 | .1988 | .5968 | 143.95 | 1.0325 | 1.0667 | 153.55 |

TABLE I (*Concluded*)

| Concns. moles per 1000 g. of water | | | | | | |
|---|---|---|---|---|---|---|
| HCl | KCl | NaCl | Λ | δ | η | Λη |
| 2.0 | 0.0 | 0.0 | 285.10 | 1.0300 | 1.1210 | .... |
| 1.6 | .4 | .0 | 254.00 | 1.0410 | 1.0972 | .... |
| 1.2 | .8 | .0 | 220.00 | 1.0514 | 1.0735 | .... |
| 0.8 | 1.2 | .0 | 183.70 | 1.0616 | 1.0506 | .... |
| .4 | 1.6 | .0 | 145.40 | 1.0717 | 1.0285 | .... |
| .0 | 2.0 | .0 | 105.80 | 1.0820 | 1.0076 | .... |
| .0 | 1.6 | .4 | 99.45 | 1.0800 | 1.0431 | .... |
| .0 | 1.2 | .8 | 93.05 | 1.0781 | 1.0811 | .... |
| .0 | 0.8 | 1.2 | 87.02 | 1.0762 | 1.1209 | .... |
| .0 | .4 | 1.6 | 81.25 | 1.0743 | 1.1632 | .... |
| .0 | .0 | 2.0 | 75.46 | 1.0722 | 1.2065 | .... |
| .4 | .0 | 1.6 | 115.14 | 1.0643 | 1.1870 | .... |
| .8 | .0 | 1.2 | 158.00 | 1.0558 | 1.1684 | .... |
| 1.2 | .0 | 0.8 | 200.90 | 1.0471 | 1.1509 | .... |
| 1.6 | .0 | .4 | 244.10 | 1.0386 | 1.1350 | .... |
| 1.2291 | .3707 | .4002 | 212.58 | 1.0484 | .... | .... |
| 0.7860 | .8199 | .3941 | 173.14 | 1.0600 | .... | .... |
| .8079 | .3878 | .8043 | 166.29 | 1.0574 | .... | .... |
| .3778 | .3667 | 1.2555 | 119.53 | 1.0663 | .... | .... |
| .4218 | .7811 | 0.7971 | 133.84 | 1.0674 | .... | .... |
| .3969 | 1.2153 | .3878 | 138.02 | 1.0698 | .... | .... |
| 3.0 | 0.0 | 0.0 | 240.40 | 1.0450 | 1.1783 | .... |
| 0.0 | 3.0 | .0 | 101.00 | 1.1188 | 1.0274 | .... |
| .0 | 0.0 | 3.0 | 67.40 | 1.1006 | 1.3453 | .... |
| 4.0 | .0 | .0 | 210.60 | 1.0590 | 1.2378 | .... |
| 3.2 | .8 | .0 | 195.51 | 1.0781 | 1.2068 | .... |
| 2.4 | 1.6 | .0 | 176.24 | 1.0981 | 1.1713 | .... |
| 1.6 | 2.4 | .0 | 153.01 | 1.1168 | 1.1341 | .... |
| 0.8 | 3.2 | .0 | 126.02 | 1.1349 | 1.0954 | .... |
| .0 | 4.0 | .0 | 96.12 | 1.1528 | 1.0570 | .... |
| .0 | 3.2 | .8 | 88.13 | 1.1498 | 1.1309 | .... |
| .0 | 2.4 | 1.6 | 80.52 | 1.1468 | 1.2118 | .... |
| .0 | 1.6 | 2.4 | 73.22 | 1.1438 | 1.3022 | .... |
| .0 | 0.8 | 3.2 | 66.30 | 1.1407 | 1.4030 | .... |
| .0 | .0 | 4.0 | 59.76 | 1.1375 | 1.5136 | .... |
| .8 | .0 | 3.2 | 89.64 | 1.1220 | 1.4484 | .... |
| 1.6 | .0 | 2.4 | 120.69 | 1.1066 | 1.3877 | .... |
| 2.4 | .0 | 1.6 | 151.91 | 1.0980 | 1.3329 | .... |
| 3.2 | .0 | 0.8 | 182.01 | 1.0750 | 1.2834 | .... |
| 2.4449 | .7888 | .7662 | 168.16 | 1.0935 | 1.2477 | .... |
| 1.6840 | .7915 | 1.5244 | 138.40 | 1.1085 | 1.2916 | .... |
| 0.8698 | 1.4879 | 1.6423 | 113.15 | 1.1266 | 1.2664 | .... |
| .8656 | 0.7636 | 2.3708 | 105.42 | 1.1239 | 1.3502 | .... |
| .8827 | 2.2355 | 0.8818 | 115.41 | 1.1286 | 1.1784 | .... |
| 1.7110 | 1.4833 | .8057 | 140.93 | 1.1113 | 1.2195 | .... |

4. The fourth method of computing the apparent equivalent conductances of mixtures at any given total concentration is expressed by the

alligative formula $\Lambda = x\Lambda' + y\Lambda'' + (1-x-y)\Lambda'''$ in which $\Lambda'$, $\Lambda''$ and $\Lambda'''$ are the equivalent conductances of the pure salts in solutions of a concentration equal to the total electrolyte concentration of the mixtures, and $x$, $y$ and $(1-x-y)$ are the mole fractions of the electrolytes present. This equation can be given graphical representation in the case of binary mixtures by straight lines.

A graphical study of the conductivity measurements shows that the curves of equivalent conductances against concentrations exhibit positive, negative and (practically) zero curvature. The equations of the preceding paragraph give rise to surfaces and curves of zero curvature only, so that such equations are inadequate for the computation of the apparent equivalent conductances of these mixtures. The equations of Method 3 have more generality, but a comparison of the values computed by their use, with the actual measurements, does not show satisfactory concordance. In fact, the equations of Method 4 apply quite well at the lower concentrations, and show a maximum deviation of 7% at the highest concentrations studied, while the equations of Method 3 seem in general less applicable, although in certain cases the agreement is fair. Curiously, these equations of Method 3 are in general more applicable to concentrated than to dilute mixtures. The ternary mixtures do not exhibit anomalous behavior at any concentrations.

**Densities.**—As was to be expected, the densities of the mixtures show only very slight variations from the densities computed by the rule of mixtures, $\delta = x\delta' + y\delta'' + (1-x-y)\delta'''$, where the $\delta$'s refer to the densities of solutions of the pure electrolytes at concentrations equal to that of the total electrolyte concentration of the mixtures, and $x$, $y$ and $(1-x-y)$ are the corresponding mole fractions of the electrolytes present. In all cases where appreciable differences between the observed and computed densities exist, the observed values are invariably the greater. This regularity of behavior for mixtures of solutions of these three electrolytes affords a strong contrast to the somewhat irregular nature of the equivalent conductance curves.

**Relative Viscosities.**—Tested by the equation, $\eta = x\eta' + y\eta'' + (1-x-y)\eta'''$, where $\eta$ is the relative viscosity of any mixture of total electrolyte concentration, $c$, whose composition is given by the mole fractions $x$, $y$ and $(1-x-y)$, and $\eta'$, $\eta''$ and $\eta'''$ are the relative viscosities of solutions of the pure salts of concentration $c$, the observed relative viscosities are consistently less in value, the percentage variation at one molal being as great as 0.25%. A somewhat more sensitive method of expressing this degree of variation is given by the equation, $\alpha = (\eta\text{calcd.} - \eta\text{obs.})/(\eta\text{obs.} - \eta\text{water})$. For 1 $M$ mixtures, the value of $\alpha$ may become as great as 0.04, while for mixtures of 0.1 $M$ and less, it is less than the experimental error.

An examination of the data of relative viscosity in terms of its reciprocal, the relative fluidity, was made but this property proved to be less amenable to treatment than did the relative viscosities.

It is exceedingly unfortunate that relative viscosities of solutions whose densities differ appreciably from that of water cannot be determined with a high degree of precision by means of an instrument such as that employed in this investigation. Measurements have been carried out upon mixtures whose total electrolyte concentrations were 4 *M*, and while they are perhaps of slight intrinsic value, they serve to show qualitatively the trend of this property at such concentrations. It is of interest to note that the curvatures of these quasi-accurate viscosity-mole-fraction curves are of the same sign as those of the curves for the 1 *M* mixtures.

In attempting to relate $\Lambda$ and $\eta$ with other measured quantities such as the concentration and the transference number, the product $\Lambda\eta$ (and in some cases the product $\Lambda\eta^n$ where $^n$ is a number less than unity) has been used by earlier investigators. The usual method of computing the value of $\Lambda\eta$ for a given mixture is expressed by the linear equation, $\Lambda\eta = x\Lambda'\eta' + y\Lambda''\eta'' + (1-x-y)\Lambda'''\eta'''$, in which $\Lambda'\eta'$, $\Lambda''\eta''$ and $\Lambda'''\eta'''$ are the equivalent-conductance–relative-viscosity products of the pure salts in solutions of a concentration equal to the total electrolyte concentration of the mixtures and $x$, $y$ and $(1-x-y)$ are the mole fractions of the electrolytes present.

The concordance between the observed and the so-calculated values of the $\Lambda\eta$ products is generally better than the agreement between the observed and calculated values of the equivalent conductances. But the agreement is proportionately less satisfactory in the 0.5 *M* solutions than in the 1.0 *M* solutions—a fact which tends to discount the value of this particular relationship.

## Summary

The densities, equivalent conductances and relative viscosities at 25° of a series of solutions of hydrochloric acid, potassium chloride and sodium chloride, and of a series of their binary and ternary mixtures of constant chloride-ion-constituent contents have been measured, and the results have been tabulated.

The densities of the mixtures of these electrolytes are a linear function of the compositions of the solution to within 2% in the cases of the most concentrated solutions (4 moles per 1000 g. of water); for solutions of strengths of one mole per thousand grams of water and of greater dilutions, the differences between the measured values of the densities and those computed by the rule of mixtures are negligible.

The equivalent conductances of the mixtures of these electrolytes can be fairly well represented by the straight-line relation, although the differences between the measured values and those computed by the rule of mixtures amount in some cases to more than 7%. Curves presenting the equivalent conductances of the mixtures as functions of their relative compositions show all modes of behavior, and any equation advanced to account quantitatively for the equivalent conductances of such mixtures must be of a power greater than linear.

The relative viscosities of the mixtures of these electrolytes are consistently less than values computed by the rule of mixtures from the relative viscosities of pure solutions of their constituent electrolytes, save in the cases of the most dilute mixtures studied, where the differences between the measured and computed values are negligible. The presentation of the relative-viscosity data in terms of its reciprocal, the relative fluidity, is less satisfactory.

The values of the $\Lambda\eta$ products of the mixtures of these electrolytes of the concentrations of 0.5 $M$ and 1.0 $M$ can be computed by the alligative formula somewhat more exactly than can the equivalent conductances of the same mixtures. For concentrations of greater magnitude, the data are not sufficiently accurate to warrant making such calculations.

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# THE ADEQUACY OF THE ASSUMPTION OF MOLECULAR AGGREGATION IN ACCOUNTING FOR CERTAIN OF THE PHYSICAL PROPERTIES OF GASEOUS NITROGEN

by

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# THE ADEQUACY OF THE ASSUMPTION OF MOLECULAR AGGREGATION IN ACCOUNTING FOR CERTAIN OF THE PHYSICAL PROPERTIES OF GASEOUS NITROGEN

BY FREDERICK G. KEYES AND ROBERT S. TAYLOR

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## Introduction

At the present time direct proof of molecular aggregation is not generally possible. Indeed, there exist no tests for conceived varieties of molecular species, particularly in the gaseous phase, when only small numbers of the polymerized molecules exist. It is of course well known that nitrogen dioxide polymerizes or associates chemically to a double species, $N_2O_4$, but in this instance a change in color attends the shift in species; moreover, the numbers of the doubled molecules are so considerable at a pressure of one atmosphere and less, that the departure from the perfect gas laws of either species is not sufficient to prevent detection of the polymerization by means of density measurements.

Acetic acid furnishes an example of a gas or vapor which presents no change in color on shift of species to double molecules, and here again the large changes in density at low pressures are satisfactorily explained on the assumption that a doubling of species exists. It is quite possible, perhaps even certain, that acetic acid vapor and other associating gases would show a change in the absorption spectrum in regions other than the visible, but investigations to determine this important fact are lacking as far as known.

The detection, in gases under considerable pressure, of small amounts of associated or aggregated molecules either double or of higher order, presents a problem of great difficulty when the attempt is made to detect the polymerized species by means of an examination of the pressure-volume-temperature data. Obviously even at atmospheric pressure, if the fraction of double molecules is small enough, the presence of the latter may be masked because of the normal departure of the simpler species from the perfect gas laws. Thus, Lewis[1] finds the assumption of association sufficient to explain the departure of the magnetic susceptibility of oxygen from Curie's law and assigns 0.0003 as the polymerized fraction at 0° and 1 atmosphere. The departure of oxygen from the perfect gas laws, however, is of the order of magnitude of 0.1% at N. T. P., so that the one double molecule in about 7000 calculated by Lewis would produce a change in density which the best gas-density determinations that have ever been made would scarcely detect.

In the case of gases under pressure, it is clear that the problem of estimating the amount of higher-order species of molecules through the pressure-volume-temperature data is beset with peculiar difficulties. To estimate accurately the degree of aggregation, there are lacking, first, certain knowledge of the equation of state of a single and invariable molecular species; second, the equation of state of a mixture of two or more different species; third, the general thermodynamic equations connecting the numbers of the different molecular species with the temperature and pressure at any pressure in the gaseous phase. For the latter, the only complete treatment developed is for perfect gases.

Investigations have been in progress for a number of years in this Laboratory dealing with these problems. Indeed, it is now believed that the assumption is warranted that for an *invariable molecular species* at not too small volumes, the equation of state[2] is

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v + l)^2} \tag{1}$$

where $\beta$, $A$, $\alpha$ and $l$ are constants. Moreover, measurements about to be published for mixtures of nitrogen and methane indicate that the same form of equation represents the observed pressures with good approximation

The development of the application of thermodynamics to reversible chemical reactions in gases has progressed but little beyond the perfect gas stage. The progress which has been made, however, cannot wholly be taken advantage of because of the almost complete state of ignorance which surrounds the problem of the theory of the temperature dependence of the specific heats of gases. Until substantial progress has been made with the latter problem no final quantitative theory of the aggregation effect is generally possible.

The important question of whether the aggregated fraction can be assumed amenable to the same thermodynamical treatment that applies to a chemical reaction in the gaseous phase can probably be answered in the

[1] Lewis, THIS JOURNAL, 46, 2027 (1924).

[2] It is perhaps apropos to refer to the opinion of van Urk that Equation 1 is similar to that suggested by Goebel. This latter equation has the form $p = [RT/(v - b_0 + b_1p)] - [a/(v - c)^2]$, where $b_0$, $b_1$, $a$ and $c$ are constants. Clearly, Equation 1 requires the pressure to increase linearly with temperature at constant volume, whereas the equation of Goebel requires a curved isometric.

affirmative. There is, however, one element of difference which is important in the quantitative sense. The ordinary chemical reaction is accompanied by a very large heat effect whereas the heat effect due to aggregation appears to be relatively small. This condition accentuates the difficulties due to the present primitive state of the theory of gaseous specific heats, for the temperature coefficient of the aggregation would be a more important factor than for a chemical reaction where the magnitude of the heat effect is sufficient to make an exact knowledge of the specific heats of the reacting molecular species far less necessary.

The influence of pressure, at constant temperature, on gaseous chemical reactions is just beginning to receive quantitative development.[3] Since in the case of the simpler gases the aggregation effect seems to be only appreciable at higher pressures, the pressure effect on the aggregation reaction becomes important. It is necessary, in this connection, that the characteristic constants of the equation of state for the aggregated species should be known to calculate the pressure coefficient. It has been found impracticable to obtain these constants directly from pressure-volume-temperature data. In the case of molecules without permanent or natural electrical moments (assuming that simple ratios exist between the constants of the unaggregated and aggregated species), it is not difficult to find by trial the magnitude at least of the $A$ and $\beta$ constants. The assumed constants combined with the constants of the unaggregated species must give both the correct pressure effect for the aggregation and also the correct pressures when used in the equation of state.

To summarize the material available for estimating the extent and nature of the aggregation effect for at least the simpler types of molecules, we have: (1) the experimental fact that as higher temperatures are approached the constant-volume pressures are increasingly linear with the temperature; (2) an equation of state of considerable accuracy which at not too small volumes requires a linear increase of pressure with temperature at constant volume; (3) experimental proof that the equation of state for binary mixtures of nitrogen and methane,[4] two representative gases of the simpler kind, is of the same form as that which applies to the pure gases.[5]

## The Equation of State for Slight Aggregation

The classical example of a simple association is that of nitrogen oxide-nitrogen tetroxide. If $y$ is the associated fraction and the perfect gas laws are assumed for both of the molecular species, the equation of state takes the form

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[3] Gillespie, This Journal, **48**, 28 (1926).

[4] Burks, *Unpublished Thesis,* Mass. Inst. Tech.

[5] If aggregated molecules actually exist in a gas one may regard the gas as a mixture of simple and aggregated molecules, each species having its appropriate constants. Experimental proof that mixtures of nitrogen and methane are representable by Equation 1 makes it appear probable that the same rules of combination of constants (in the mixture's equations of state) hold also for aggregated and unaggregated species.

$$p = (RT/v)\ (1 - y/2) \tag{2}$$

The isometric corresponding to this equation will evidently tend to linearity at high temperatures (assuming that nitrogen dioxide does not decompose) where the pressure is substantially $p = RT/v$. As the temperature falls, however, the pressures become increasingly less than those corresponding to the extrapolation of the linear high-temperature portion until substantially complete association is attained, when the pressure tends again to be linear with temperature and pressure given by the equation $p = (^1/_2\, RT)/v$.[5]

The constants of the equation of state for the two species in the example chosen are not known but if they were known the equation of state would be, from Equation 1,

$$p = \frac{RT(1 - y/2)}{v - \delta_y} - \frac{A_y}{(v + l_y)^2} \tag{3}$$

where $\delta_y$ is written for the quantity $\beta_y e^{-\frac{\alpha_y}{v}}$ corresponding to an associated fraction $y$ and similarly for the remaining quantities $A_y$ and $l_y$.[6]

Equation 3, while complicated, takes on a simple form where the associated fraction is small, particularly if the pressure is low (less than several atmospheres)—for the variation of the constants $\delta_y$, $A_y$, $l_y$ are then of higher order as compared with $R(1 - y/2)$. Equation 3 under these simplifying conditions becomes, where $A_1$, $\delta_1$, $l_1$ pertain to the simple species,

$$p = \frac{RT\ (1 - y/2)}{v - \delta_1} - \frac{A_1}{(v + l_1)^2} \tag{4}$$

The fraction associated by the known perfect gas law thermodynamic development is

$$\frac{y}{(1 - y)^2} = gf(T)\,\frac{1}{v} \tag{5}$$

where $g$ is a constant and $f(T)$ is $e^{\frac{2\Delta U}{RT}}$, provided differences in heat capacities of the two reacting species are neglected.

Equation 4 may be readily expanded in a series of reciprocal volumes resulting in the equation

$$pv = RT\left[1 + \left(\beta + \frac{A}{RT} - \frac{gf(T)}{2}\right)\frac{1}{v} + \left(\beta^2 - \alpha\beta + \frac{2Al}{RT} - \frac{gf(T)}{2}\,\beta\right)\frac{1}{v^2} + \dots\right] \tag{6}$$

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[6] If, for example, the $\beta$ constant for the unaggregated species is designated $\beta_1$ and the aggregated type molecules $\beta_2$, $\beta_y$ might be given by the equation $\beta = \beta_1\ (1 - y) + \beta_2 y$. This proves to be the case in the nitrogen-methane mixtures. The $A_y$, judged by analogy with the nitrogen-methane mixtures, would be $A_y = [\sqrt{A_1}(1 - y) + \sqrt{A_2}\,y]^2$ while $\alpha_y$ and $l_y$ would be of a form similar to that given for $\beta_y$. The fraction associated, $y$, is a function of both volume and temperature and it is therefore clear that $A_y$, $\delta_y$ and $l_y$ are volume and temperature functions.

where $gf(T)$ $(1/v)$ has been substituted for $y$ from Equation 5 on the assumption that $y$ is small. If $y$ should prove to be large, this approximation should, of course, be corrected by using in the $B$ coefficient $gf(T)/(1-y)^2v$. For nitrogen the approximation $gf(T)$ $1/v$ appears to be sufficient to represent $y$ although where larger values of $y$ are needed Equation 5 must be employed.

The actual observations pertaining to a gas may be represented by a reciprocal volume series of the form

$$pv = RT\left(1 + B\frac{1}{v} + C\frac{1}{v^2} + \ldots\ldots\right) \tag{7}$$

The coefficient $B$ may, therefore, be identified with $[\beta - A/RT - gf(T)/2]$ from Equation 6, which graphically is the slope of the $pv$ isotherm at $p = 0$. The coefficient $C$, which is more complicated in form, need not be discussed explicitly since the values of $C$ available are not known with sufficient accuracy at the present time to make profitable their use according to the methods to be developed in the present paper.

The quantity $f(T)$ in the form $e^{\frac{2\Delta U}{RT}}$ would become unity at $T = \infty$. On the other hand, $f(T)$ becomes increasingly large as $T$ diminishes. The coefficient $B$, accepting $f(T)$ as of form $e^{\frac{2\Delta U}{RT}}$, is thus linear in reciprocal $T$ at sufficiently high temperatures and increasingly concave to the axis of abscissas, $1/T$, at lower temperatures.

It is important to note that in the absence of double molecules, an association of three of the simpler molecules to triple molecules would leave the $B$ coefficient simply $(\beta - A/RT)$, since $z$, the fraction of triple molecules, for small values of $z$, varies as the reciprocal volume squared, thus first appearing in the coefficient $C$.

In what follows it will be assumed that if aggregation to double molecules takes place in a gas, Equation 4 applies (aggregation small). The form of $f(T) - e^{\frac{2\Delta U}{RT}}$, similar in form to that pertaining to an ordinary chemical association of perfect gases wherein the heat capacities of the two species of molecules are supposed equal, will also be assumed to apply to the case of aggregation. These simplifying conditions form the basis for a preliminary treatment, having been found to be sufficient to indicate semi-quantitatively the nature of the effects to which the assumption of aggregation leads.

## The Experimental Data for Nitrogen

There now exists a considerable amount of pressure-volume-temperature data for nitrogen from temperatures of about —146° to 400°. The bulk of low-temperature data is due to A. Th. van Urk,[7] and recently Smith and

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[7] Van Urk, *Thesis,* Leiden, 1924; *Proc. 4th. Int. Congress Refrigeration,* **1,** 75 (1924).

Taylor[8] have published measurements of pressure and temperature for various constant volumes from 23 cc. per g. The data above 200° are due to Holborn and Otto,[9] as well as other data in the interval of 0° to 200°, and recently additional data below zero have been published by the latter.

With the exception of the data due to Smith and Taylor all the experimental material was obtained from measurements of pressure and volume at constant temperature. Holborn and Otto's results are correlated at each temperature by means of equations of the form of 7. Van Urk, however, gives no similar equations for his data below zero. The data have, therefore, been correlated by means of quadratic equations in reciprocal volume. In determining the coefficients, $RT$ as well as $B$ and $C$ may be regarded as a coefficient to be determined from the data. On the other hand, since $R$ is known, $RT$ may be computed for each temperature and the quadratic equations reduced to linear equations in density. The constants for both procedures are given in Table I. The $B$ coefficients determined by the method of computing $RT$ appear to vary most regularly with temperature. The observational data are about equally well represented (1 part per 1000) by either formulation to volumes of 10 cc. per g.

TABLE I

DATA OF VAN URK FOR NITROGEN

I, coefficients of equation $pv = a + b(1/v) + c(1/v^2)$; II, coefficients of equation $pv = rT + b'(1/v) + c'(1/v^2)$; $r = 2.9286/799.55$; $M = 28.02$; $R = 82.058$; $T = 273.13 + t$.

| | I | | | II | | |
|---|---|---|---|---|---|---|
| $t$ | $a$ | $\frac{c}{a} \times 10^6$ | $B$ or $\frac{b}{a} \times 10^3$ | $rT$ | $\frac{c'}{rT} \times 10^6$ | $B'$ or $\frac{b'}{rT} \times 10^3$ |
| − 23.62 | 0.91191 | 2.12494 | 0.65225 | 0.91392 | 3.3438 | 0.7599 |
| − 50.26 | .82466 | 5.86276 | 1.46130 | .81634 | 2.6558 | 1.1025 |
| − 81.10 | .70870 | 5.16802 | 1.96441 | .69972 | 2.4438 | 1.6007 |
| −102.25 | .62975 | 5.13793 | 2.49445 | .62592 | 3.7626 | 2.3183 |
| −121.19 | .55298 | 4.07217 | 2.95527 | .55653 | 5.1499 | 3.1045 |
| −131.27 | .51911 | 5.72218 | 3.59236 | .51949 | 5.7616 | 3.6022 |
| −141.53 | .48267 | 6.64502 | 4.24466 | .48203 | 6.5597 | 4.2251 |
| −144.46 | .47166 | 6.91246 | 4.44429 | .47130 | 6.8385 | 4.4306 |
| −146.32 | .46534 | 7.06050 | 4.58300 | .46448 | 7.0530 | 4.5750 |

The unit of pressure is the atmosphere of 76 cm. of mercury at 0°; the unit of volume is the volume of 1 g. of the gas at 0° and 1 atm. (799.55 cc. per gram).

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[8] Smith and Taylor, THIS JOURNAL, 45, 2107 (1923). Van Urk has called attention in his dissertation to the fact that the $pv$ isotherm for 0°, taken from Smith and Taylor's data, is about 0.5% lower than this isotherm, as measured by both van Urk and Holborn and Otto. Smith and Taylor have since found that an error of about this magnitude was made in computing the amount of nitrogen introduced into their piezometer [*ibid.*, **48**, 3122 (1926)].

[9] Holborn and Otto, *Z. Physik*, **10**, 367 (1922); **23**, 77 (1924); **30**, 320 (1924); **33**, 1 (1925).

In Table II will be found a list of the coefficients corresponding to temperatures from 400° to —146.32°. The numbers in the last column designate the reference to the literature from which the coefficients $B$ were taken. The coefficients at round temperatures, —50°, —100°, —130°, are coefficients of $p$ from empirical equations for $pv$ of the form $a + b'p + c'p^2$ given by Holborn and Otto.

TABLE II

EQUATIONS FOR ISOTHERMS

Pressure in atmospheres, volume in "Amagat Units" or the volume at 0° and 1 atm. taken as the volume unit.

| Temp., °C. | $a$ or $RT$ | $B_{\text{obs.}} \times 10^3$ | $B_{\text{calcd.}}$ | $C \times 10^6$ | Observer, Ref. |
|---|---|---|---|---|---|
| 400 | 2.46523 | +1.04694 | 1.1420 | 2.51379 | *b* |
| 300 | 2.09905 | +0.91733 | 0.9562 | 2.01090 | *b* |
| 200 | 1.73285 | + .67840 | .6897 | 2.39479 | *b* |
| 150 | 1.54975 | + .50839 | .5080 | 2.48681 | *b* |
| 100 | 1.36664 | + .26641 | .2763 | 2.87953 | *b* |
| 50 | 1.18352 | − .01670 | − .0301 | 2.74274 | *b* |
| 0 | 1.00046 | − .45516 | − .4561 | 3.03602 | *b* |
| 100 | 1.36661 | + .26609 | + .2763 | 2.87617 | *a* |
| 50 | 1.18351 | − .02493 | − .0301 | 2.76710 | *a* |
| 0 | 1.00046 | − .43386 | − .4561 | 2.64643 | *a* |
| 20 | 1.07370 | − .24448 | − .2673 | 2.32840 | *c* |
| 0 | 1.00041 | − .40996 | − .4561 | 2.06556 | *c* |
| − 23.62 | 0.91392 | − .7599 | − .7229 | 3.3438 | *d* |
| − 50.26 | .81634 | −1.1025 | −1.1004 | 2.6558 | *d* |
| − 81.10 | .69972 | −1.6007 | −1.6961 | 2.4438 | *d* |
| −102.25 | .62592 | −2.3183 | −2.2704 | 3.7626 | *d* |
| −121.19 | .55653 | −3.1045 | −2.9936 | 5.1499 | *d* |
| −131.27 | .51949 | −3.6022 | −3.5168 | 5.7616 | *d* |
| −141.53 | .48203 | −4.2251 | −4.2162 | 6.5597 | *d* |
| −144.46 | .47130 | −4.4306 | −4.4574 | 6.8385 | *d* |
| −146.32 | .46448 | −4.575 | −4.6237 | 7.0530 | *d* |
| − 50 | .... | −1.177 | −1.0962 | .... | ... |
| −100 | .... | −2.315 | −2.2010 | .... | ... |
| −130 | .... | −3.561 | −3.4444 | .... | ... |

[a] Holborn and Otto, *Z. Physik*, **10**, 367 (1922).

[b] Holborn and Otto, *ibid.*, **23**, 77 (1924).

[c] Van Urk, *Thesis*, Leiden, 1924.

[d] Van Urk data constants computed by Keyes and Taylor.

Fig. 1 gives a graphic representation of the data contained in Table II. In this representation $B$ is plotted with $1/T$ as abscissas. It is evident that the general prediction based on $B$ represented by $[\beta - A/RT - gf(T)/2]$ is fulfilled.

## Discussion of the Relation between $B$ and the Temperature

The quantity $f(T)$ is of a mathematical form which makes it impractical to attempt to determine the four constants $\beta$; $A$, $g$ and $\Delta U$ directly by ordinary methods. The treatment of the constant-volume pressures and temperatures between 0° and 200° has shown that the magnitudes of the $\beta$ and $A$ constants of the equation of state are approximately $\beta = 1.7$ and $A = 1650$. By trial it was found that $\beta = 1.768$, $A = 1643$, $g = 0.016378$ (in cc. per g. units), and $\Delta U = 614$ cal. represent the $B$ coefficients as well as may be expected in view of the simplicity of $f(T)$. Equation 5 in the form $\log y/(1 - y)^2$ is the most convenient to use in computations and follows.

$$\log_{10} \frac{y}{(1 - y)^2} = \frac{266.9}{T} - 1.7858 - \log_{10} v \text{ cc./g.} \tag{8}$$

The constants $g$ and $\Delta U$ were determined, as already stated, on the assumption that $y$ as it enters the $B$ coefficient was small enough to be assumed equivalent to $y/(1 - y)^2$. The value of $y$ from $y/(1 - y)^2$ even at —150° (0.0032) is greater than $y$ by only 1 part in 156.

In units based on the volume of 1 g. of nitrogen at zero taken as unity,[10] the pressure being in atmospheres, there results the following equation for $B$.

$$B = 0.002211 - \frac{0.702}{T} - \frac{2.0483 \times 10^{-5}}{2} e^{614/T} \tag{9}$$

Col. 3 of Table II contains computed values of $B$ in Amagat units. In Fig. 1, the full line through the observational data was computed from Equation 9 while the straight line above the data represents the first two terms of the right-hand member of Equation 9. The agreement of the computed and observed data is sufficient to indicate that the assumption of aggregation suffices to reproduce the general characteristics of the relation between $B$ and the temperature.

The higher temperatures 400°, 300° and 200° indicate a trend away from the linear portion of the curve between 0° and 150° which is not reproduced by Equation 9. There is, of course, no difficulty in giving to $f(T)$ a form which will reproduce the curvature indicated by the observations at the higher temperatures. It appears best, however, to postpone such an attempt until an increased knowledge of aggregation in gases has either indicated or definitely excluded the possibility of such an effect accompanying aggregation. The simple form here used for $f(T)$ reduces substantially to unity at higher temperatures and $A/RT$ vanishes leaving $(\beta - g)$, a constant independent of temperature, for the $B$ coefficient.[11]

Fig. 1 has been used to insert the Holborn and Otto $B$ coefficients for argon. It will be observed that the general trend of the data is identical with that of nitrogen, except that there is no tendency for the 300° and 400° $B$ values to depart from the nearly linear course shown by the $B$ values from 0° to 200°. On the other hand the $A/R$ value for argon is somewhat larger than for nitrogen and a higher temperature may be required to disclose a trend in the high-temperature $B$ value similar to that of nitrogen. Hydrogen, helium and neon, all of which have small values of $A/R$,

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[10] The unit of volume in terms of the volume of a gram of gas in cc. at N. T. P. will be referred to hereafter as the "Amagat unit."

[11] Helium has a very small $A/R$ value (in Amagat units about 0.014 as compared with 0.702 for nitrogen) and $B$ would vary but little from constancy (1%) above zero.

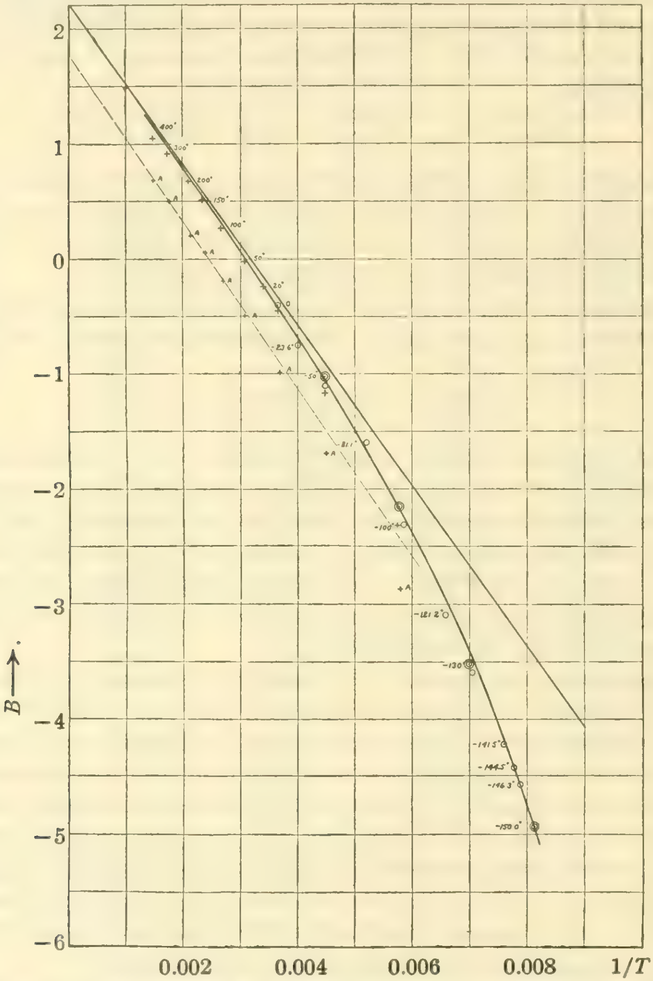

Fig. 1.—$B$ coefficients for nitrogen. +, Holborn and Otto. ⊙, van Urk. ◉, Onnes.

show the high-temperature curvature effect that nitrogen does, but the detailed discussion of these substances will find more suitable place in another paper. For the present, it is clear that the general course of the dependence of the $B$ coefficient on temperature has been accounted for on a rational basis and that further knowledge of the properties of aggregated molecules must be awaited before a finally satisfactory quantitative theory can be concluded.

## The Comparison of the Observed and Computed Pressures

The usual procedure followed to obtain the approximate values of the equation of state constants $A$, $\beta$, $\alpha$ and $l$ of Equation 1 has been to employ data pertaining to as high temperatures as possible, ignoring the slight actual curvature of the isometrics. By this compromise it is possible to represent the observational data with very satisfactory accuracy, provided the curvature is small. Some years ago, however,[12] the desirability of finding means of estimating the aggregation was suggested. The present paper indicates one method based on the $B$ coefficients and Equations 4 and 5. An earlier paper[13] showed that the Joule-Thomson data in its relation to temperature at low pressures could be accounted for on the hypothesis of aggregation using Equations 4 and 5, thereby giving a means of estimating the amount of supposed aggregation. The long range of data for nitrogen offers an opportunity of testing how well the actual curvature of the isometrics of nitrogen are reproduced when the aggregation effect is included in the equation of state.

The values of $\beta$ and $A$ ($\beta = 1.768$; $A = 1643$ in cc. per g. atm. units) have already been determined from the $B$ coefficients. Emphasis has already been put on the fact that these constants, in the absence of $B$ coefficients of the highest accuracy, can be only approximate (unless by chance 1 or 2% of the true values). The values of $\alpha$ and $l$ might be determined from the $c$ coefficients but the relation of these data to the temperature is too erratic to be used for the purpose. The values of $\alpha$ and $l$ were, therefore, assumed to complete the constants of Equation 1. This was made possible from equations of state of Form 1 which have been used to represent data for nitrogen wherein the curvature of the isometrics was neglected. The equation assumed to calculate the pressures is as follows.

$$p_{\text{atm.}} = \frac{2.9286\ T\left(1 - \frac{y}{2}\right)}{v - 1.768\ e^{-1.082/v}} - \frac{1643}{(v + 0.22)^2} \tag{10}$$

When aggregation is assumed absent this becomes

$$p_{1\ \text{atm}} = \frac{2.9286\ T}{v - 1.768\ e^{-1.082/v}} - \frac{1643}{(v + 0.22)^2} \tag{11}$$

Equation 5[14] will be used for computing $y$ and in Table III are listed the pressures computed by Equation 10 and observed for the constant volumes 26.651, 19.989, 13.326 and 10.661 cc. per gram, corresponding to densities 75, 60, 40 and 30 in the Amagat volume units. These observed pressures were interpolated by means of the isothermal-density-series equations given by Holborn and Otto and similar equations relative to temperatures below zero for van Urk's data, using the coefficients given in Table I. The third horizontal row corresponding to each volume likewise contains the pressure diminution assumed to be due to aggregation, namely, $[2.9286T/(v - \delta)](y/2)$, and the last row the difference between the pressure given by Equation 11 and the observed pressure. The two latter quantities should be equal for exact agreement of the observed pressures and those given by Equation 10.

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[12] Keyes and Felsing, THIS JOURNAL, **41**, 589 (1919).

[13] Keyes, *ibid.*, **46**, 1584 (1924).

[14] It is convenient to make a plot of $y/(1 - y)^2$ and $y$ which may be used to expedite computations of $y$ from equations of this kind.

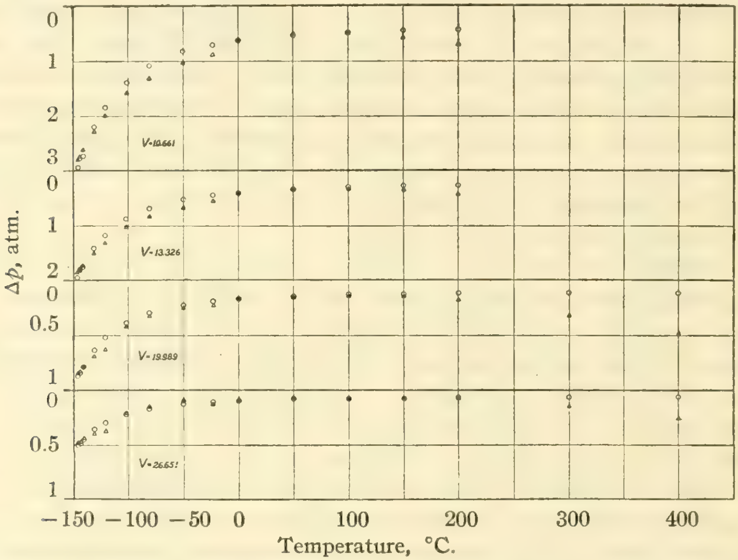

Fig. 2.—Deviations from linearity of nitrogen isometrics; ○, calculated; Δ, van Urk; Holborn and Otto.

Fig. 2 is a graphic representation of the departure of both these observed and computed pressure differences, indicating that the departure from linearity of each isometric is reproduced in its general features by Equation 10. The three highest temperatures indicate an increase of the pressure differences given by subtracting the observed pressures from Equation 11. This effect might be explained by failure of the equation used to calculate $y$ (Equation 8). Nevertheless, it would seem to require for its explanation on the aggregation hypothesis an increase in $y$ at higher temperatures. Further measurements at 200° and higher temperatures, together with a more exact knowledge of the relation of aggregation to temperature, may be expected to explain the failure of the isometrics to remain linear after attaining substantial linearity between 0° and 150°.

### TABLE III

COMPARISON OF THE PRESSURES OF NITROGEN WITH THOSE COMPUTED BY EQUATION 11

Unit of pressure 76 cm. of Hg at 0°

| | −146.32° | −144.46° | −141.53° | −131.27° | −121.19° | −102.25° | −81.1° | −50.26° |
|---|---|---|---|---|---|---|---|---|
| | | | | $v$ = 10.661 cc. per g. | | | | |
| Press., Eq. 10 | 24.160 | 24.943 | 25.923 | 29.772 | 33.371 | 39.943 | 47.087 | 57.308 |
| Press., obs. | 24.290 | 24.958 | 26.029 | 29.697 | 33.231 | 39.761 | 46.868 | 57.110 |
| Eq. 11 − Eq. 10 | 2.926 | 2.757 | 2.724 | 2.190 | 1.848 | 1.395 | 1.086 | 0.832 |
| Eq. 11 − press. obs. | 2.796 | 2.742 | 2.618 | 2.265 | 1.988 | 1.577 | 1.306 | 1.030 |
| | | | | $v$ = 19.989 cc. per g. | | | | |
| Press., Eq. 10 | 20.861 | 21.479 | 22.269 | 25.161 | 27.917 | 32.957 | 38.444 | 46.329 |
| Press., obs. | 20.953 | 21.457 | 22.277 | 25.075 | 27.782 | 32.829 | 38.301 | 46.186 |
| Eq. 11 − Eq. 10 | 1.937 | 1.785 | 1.728 | 1.405 | 1.173 | 0.876 | 0.685 | 0.522 |
| Eq. 11 − press. obs. | 1.845 | 1.807 | 1.720 | 1.419 | 1.308 | 1.004 | .828 | .665 |
| | | | | $v$ = 13.326 cc. per g. | | | | |
| Press., Eq. 10 | 15.386 | 15.714 | 16.234 | 18.031 | 19.756 | 22.917 | 26.389 | 31.392 |
| Press., obs. | 15.412 | 15.721 | 16.234 | 17.971 | 19.649 | 22.887 | 26.355 | 31.368 |
| Eq. 11 − Eq. 10 | 0.869 | 0.839 | 0.787 | 0.631 | 0.518 | 0.385 | 0.296 | 0.224 |
| Eq. 11 − press. obs. | .843 | .832 | .787 | .691 | .625 | .418 | .330 | .248 |
| | | | | $v$ = 26.651 cc. per g. | | | | |
| Press., Eq. 10 | 12.100 | 12.341 | 12.817 | 14.015 | 15.260 | 17.559 | 20.090 | 23.751 |
| Press., obs. | 12.130 | 12.351 | 12.723 | 13.975 | 15.719 | 17.566 | 20.107 | 23.785 |
| Eq. 11 − Eq. 10 | 0.504 | 0.481 | 0.449 | 0.355 | 0.292 | 0.216 | 0.166 | 0.124 |
| Eq. 11 − press. obs. | .474 | .471 | .443 | .395 | .373 | .209 | .149 | .090 |

| | −23.62° | 0° | 50° | 100° | 150° | 200° | 300° | 400° |
|---|---|---|---|---|---|---|---|---|
| | | | | $v$ = 10.661 cc. per g. | | | | |
| Press., Eq. 10 | 66.043 | 73.758 | 90.005 | 106.211 | 122.403 | 138.582 | .... | ..... |
| Press., obs. | 65.865 | 73.750 | 90.023 | 106.206 | 122.289 | 138.327 | .... | ..... |
| Eq. 11 − Eq. 10 | 0.704 | 0.622 | 0.527 | 0.481 | 0.449 | 0.430 | .... | ..... |
| Eq. 11 − press. obs. | .882 | .630 | .509 | .494 | .571 | .693 | .... | ..... |
| | | | | $v$ = 19.989 cc. per g. | | | | |
| Press., Eq. 10 | 53.083 | 59.046 | 71.628 | 84.177 | 96.708 | 109.249 | .... | ..... |
| Press., obs. | 52.992 | 59.044 | 71.640 | 84.159 | 96.654 | 019.099 | .... | ..... |
| Eq. 11 − Eq. 10 | 0.439 | 0.390 | 0.328 | 0.298 | 0.278 | 0.267 | .... | ..... |
| Eq. 11 − press. obs. | .530 | .392 | .315 | .316 | .332 | .417 | .... | ..... |
| | | | | $v$ = 13.326 cc. per g. | | | | |
| Press., Eq. 10 | 35.688 | 39.485 | 47.508 | 55.517 | 63.521 | 71.521 | 87.516 | 103.507 |
| Press., obs. | 35.649 | 39.490 | 47.517 | 55.500 | 63.497 | 71.460 | 87.313 | 103.135 |
| Eq. 11 − Eq. 10 | 0.188 | 0.168 | 0.141 | 0.127 | 0.118 | 0.114 | 0.110 | 0.110 |
| Eq. 11 − press. obs. | .227 | .163 | .132 | .144 | .142 | .175 | .313 | .482 |
| | | | | $v$ = 26.651 cc. per g. | | | | |
| Press., Eq. 10 | 26.897 | 29.679 | 35.560 | 41.435 | 47.307 | 53.175 | 64.911 | 76.645 |
| Press., obs. | 26.874 | 29.695 | 35.571 | 41.433 | 47.306 | 53.156 | 64.822 | 76.447 |
| Eq. 11 − Eq. 10 | 0.104 | 0.093 | 0.078 | 0.070 | 0.065 | 0.063 | 0.060 | 0.060 |
| Eq. 11 − press. obs. | .127 | .077 | .067 | .072 | .066 | .082 | .149 | .258 |

It is quite evident that very exact agreement between the observed and computed pressures may be obtained by modifying Equation 8. This has not been done in the present paper since it would contribute little or nothing to the examination of the usefulness or theory of the aggregation hypothesis, especially since the variation of the constants with association has been altogether neglected.

An equation reproducing the pressure observations of Holborn and Otto with substantial accuracy from 0° to 200° may be obtained by neglecting the slight curvature of the isometrics. Such an equation follows.

$$p = \frac{2.9286T}{v - 1.766\, e^{-1.065/v}} - \frac{1687.1}{(v + 0.136)^2} \qquad (12)$$

Table IV gives a survey of the agreement realized between the pressures computed by Equation 12 and the observed pressures.

TABLE IV

PRESSURES COMPUTED BY EQUATION 13 COMPARED TO HOLBORN AND OTTO OBSERVATIONS

| Vol., cc./g. | | 0° | 50° | 100° | 150° | 200° |
|---|---|---|---|---|---|---|
| 40 | Obs. | 19.84 | 23.68 | 27.50 | 31.32 | 35.14 |
| | Calcd. | 19.848 | 23.673 | 27.499 | 31.324 | 35.149 |
| 30 | Obs. | 26.40 | 31.62 | 36.76 | 41.94 | 47.10 |
| | Calcd. | 26.411 | 31.586 | 36.761 | 41.936 | 47.111 |
| 25 | Obs. | 31.63 | 37.99 | 44.21 | 50.55 | 56.76 |
| | Calcd. | 31.648 | 37.931 | 44.214 | 50.496 | 56.779 |
| 20 | Obs. | 39.46 | 47.49 | 55.47 | 63.50 | 71.43 |
| | Calcd. | 39.486 | 47.478 | 55.468 | 63.459 | 71.449 |
| 15 | Obs. | 52.49 | 63.52 | 74.47 | 85.43 | 96.34 |
| | Calcd. | 52.526 | 63.490 | 74.454 | 85.418 | 96.382 |
| 10 | Obs. | 78.63 | 96.16 | *113.61*[a] | *130.92*[a] | *148.20*[a] |
| | Calcd. | 78.640 | 96.151 | *113.559*[a] | *130.966*[a] | *148.374*[a] |

[a] Extrapolated by means of the empirical $pv$ equations.

On the other hand, the pressures computed by Equation 12 at 300° and 400° are always higher than the observations of Holborn and Otto. For example, at 40 cc. per gram and 400° the calculated pressure is one part in 300 greater than the observed pressures, and at 300° one part in 510.

## The Heat Capacity at Constant Volume

The heat capacity of a gas at constant volume would be dependent upon the temperature alone if Equation 1 were the true equation of state. The existing observational material indicates, however, that in general this property is a function of the density as well as of temperature. As higher temperatures are approached, the constant-volume heat capacity becomes an increasingly less pronounced function of the density, as would be inferred from the fact that $(\partial p/\partial T)_v$ tends to become constant at higher temperature.

Aggregation, if it exists in a gas, would be a very important factor in contributing a heat effect to the gas since heating at constant volume diminishes the aggregated fraction with attendant heat absorption. Moreover, this effect would be considerable for the heat of aggregation is enormous relative to the normal heat capacity of the molecules *per se*.

The calculation of this effect presents no difficulties, although for making numerical calculation there is a paucity of data which is much to be regretted. The use of Equation 2 in connection with the thermodynamical equation $(\partial C_v/\partial_v)_T = T(\partial^2 p/\partial T^2)_v$ leads easily to the following equation, assuming that $y$ is sufficiently small to identify $y/(1-y)^2$ with $y$.

$$C_v = \text{constant} + 2\,Ry(\Delta U/RT)^2 \tag{13}$$

When $T$ is infinite $C_v = \text{constant} = C_{v_1}$ and the contribution to the specific heat at constant volume due to aggregation to double molecules would on this basis be

$$C_v - C_{v_1} = \Delta C_v = 2\,Ry(\Delta U/RT)^2 \tag{14}$$

The phenomenological equation for $Cv$ per unit mass of substance would be, on the assumption to double molecules only,

$$C_v = C_{v_1}\,(1-y) + C_{v_2}y + (-\Delta U)\,(\partial y/\partial T)_v \tag{15}$$

where $Cv_1$ is the heat capacity *per se* of the single molecules and $C_{v_2}$ that of the double molecules, the fraction associated being $y$. Using Equation 5, there results

$$C_v = C_{v_1} + (C_{v_2} - C_{v_1})\,y + 2\,Ry\,\frac{1+y}{1-y}\left(\frac{\Delta U}{RT}\right)^2 \tag{16}$$

This equation is of course identical with Equation 14 for $y = 0$.

There are unfortunately no experimental data bearing on $C_{v_2}$ for any substance. The assumption will be made, however, that $C_{v_1}$ is equal to $C_{v}$. for aggregation and Equation 16 becomes

$$C_v = C_{v_1} + 2\,Ry\,\frac{1-y}{1+y}\left(\frac{\Delta U}{RT}\right)^2 \tag{17}$$

There are no data available for the constant-volume heat capacity of pure nitrogen. Jakob, however, has computed the specific heat at constant volume for air, using the experimentally measured constant pressure-specific heat capacity of air to 200 atm. at 59° by Holborn and Jakob[15] and an empirical equation of state for air representing the measurements of Holborn and Otto[9] on the pressure-volume-temperature properties.

In addition to these computations further computations based on the interpretation of the Joule-Thomson measurements of Bradley and Hale,[16] Noell,[17] and Jakob,[18] were employed to compile a table of the most probable values of the heat capacities at constant pressure and at constant volume from temperatures of −79.3° to 250° and over a pressure range from 0 to about 200 atmospheres.

In the absence of specific-heat data on pure nitrogen it is of interest to employ Equation 17 to compute the heat capacities of air, using Equation 8 for the supposed aggregation of nitrogen. The "computed" heat capacities employ for $C_{v_1}$ the heat capacity of air at zero pressure which is given by Jakob as 0.172 cal. per gram from —79.3° to 50°. Table V gives the calculated numbers together with the Jakob values corresponding to 0,° —50 and —79.3° at several pressures to 193.55 atmospheres. Col. 4, $\Delta C_v$, gives the amount by which $C_{v_1}$ increases as the pressure increases.

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[15] Holborn and Jakob, *Z. Techn. Physik*, **4**, 465 (1923).

[16] Bradley and Hale, *Phys. Rev.*, **29**, 258 (1909).

[17] Noell, *Z. Ver. deut. Ing.*, **62**, 49 (1918).

[18] Jakob, *Fortschritte Arb. Ver. deut. Ing.*, No. 202, 1917.

Table V

$C_v$ as Function of the Pressure

| Temp., °C. | Pressure, atm. | $y$ | $\Delta C_v$, calcd. | $C_v$, calcd. | $C_v$, Jakob |
|---|---|---|---|---|---|
| 0 | 1 | 0.00019 | 0.0000 | 0.172 | 0.172 |
| | 48.39 | .0095 | .0017 | .174 | .175 |
| | 96.78 | .0185 | .0032 | .175 | .178 |
| | 145.17 | .027 | .0046 | .177 | .179 |
| | 193.55 | .051 | .0082 | .180 | .181 |
| −50 | 0.0 | .0000 | .0000 | .172 | .172 |
| | 48.39 | .0195 | .005 | .177 | .178 |
| | 96.78 | .0390 | .010 | .182 | .182 |
| | 145.17 | .0542 | .013 | .185 | .186 |
| | 193.55 | .067 | .016 | .188 | .188 |
| −79.3 | 0.0 | .0000 | .0000 | .172 | .172 |
| | 48.39 | .036 | .012 | .184 | .185 |
| | 96.78 | .070 | .022 | .194 | .196 |
| | 145.17 | .098 | .029 | .201 | .206 |
| | 193.55 | .117 | .033 | .205 | .215 |

It is evident from Table V that the relation of $C_v$ to both pressure and temperature is given by Equation 17 as accurately as could have been expected. Indeed, it is anticipated that extended data bearing on the heat capacities of gases at constant volume will provide excellent data with which to test the value of the aggregation hypothesis.

## Concluding Comments

Notwithstanding the tolerable agreement between observational material and computation disclosed in the present paper, it is well to emphasize that the existence of definite molecular aggregates is scarcely proved. Indeed, the treatment of aggregation adopted may be regarded from a theoretical point of view as defective since there is doubt that the mass law holds for aggregation which, at least for substances of the class of nitrogen, must be regarded as of purely electrical origin. However, even were the mass law applicable, the dependence of the aggregation on temperature and volume as given by the perfect gas treatment would be deficient at the comparatively high pressures here considered.

Moreover, disregarding all these disabilities of the treatment, there remains from the strictly theoretical point of view the important omission to allow for the variation of the fundamental constants $A$, $\beta$, $\alpha$ and $l$ of the equation of state due to aggregation. The theory of the origin of the cohesive forces is sufficient to lead to a plausible inference concerning the ratios of the $A$ constants and possibly also the $\beta$ constants for definitely associated double and single molecules.

In the main, reliance for further information regarding aggregation must be placed on comparison, in addition to $p$-$v$-$T$ data, of the variation of viscosity, dielectric constant, refractive index, absorption of light, and the Kerr effect with both temperature and pressure. Specific-heat data at constant volume are also valuable for the purpose although the technique of the measurement of this quantity has not as yet been finally worked out.

## Summary

1. The attempt has been made to use the hypothesis of molecular aggregation in connection with the equation of state $p = (RT/v - \delta) - A/(v + l)^2$ to explain the observed dependence of the coefficient of $1/v$ in the virial equation on the temperature as well as the curvature of the isometrics at low temperatures in the case of nitrogen.

2. The dependence of the supposed aggregation on volume and temperatures has been assumed to conform to the mass law—perfect gas treatment used in discussing chemical equilibria, assuming the heat capacities of the simple and aggregated species to be the same per unit mass.

3 The aggregation equation for nitrogen has been obtained from the coefficient [$B$ coefficient] of $1/v$, and also the values of $\beta$ and $A$ of the equation of state (1). The dependence of the $B$ coefficients on temperature is represented in its general characteristics. The temperature trend, however, of the $B$ coefficients due to Holborn and Otto at 300° and 400° is not exactly reproduced and in fact appears difficult to account for unless aggregation is related to temperature and volume otherwise than as herein assumed.

4. A comparison has been made of the observed isometric pressures for nitrogen with those calculated by means of the aggregation equation (8) combined with an approximate equation of state for the unaggregated species. It is shown that the curvature of the isometrics is reproduced except at 300° and 400°.

5. The aggregation equation (8) for nitrogen has been used to compute the constant-volume heat capacities of air as a function of the pressure. Good agreement is found between the observed and computed values.

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# THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS.

## IV. THE TRANSFERENCE NUMBERS OF SOME CHLORIDE SOLUTIONS

by

E. R. Smith and D. A. MacInnes

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# THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. IV. THE TRANSFERENCE NUMBERS OF SOME CHLORIDE SOLUTIONS

By E. R. Smith and D. A. MacInnes

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In the earlier articles of this series[1] two forms of apparatus for measuring transference numbers by the method of moving boundaries were described, neither of which was entirely satisfactory. In the first form the electrodes were apparently too near the calibrated tube through which the boundary sweeps. The second form, which was otherwise properly designed, was constructed on too large a scale, and gave difficulty due to the heating effects of the current passing through the apparatus. In this article an apparatus is described which is satisfactory both in design and dimensions. Also, results are given of measurements, made with the new apparatus, of the transference numbers of solutions of potassium chloride, sodium chloride and of hydrochloric acid.

The equation for the transference number from the movement of a single boundary[1] and the correction, first pointed out by G. N. Lewis,[2] can be conveniently combined into the formula

$$T = \frac{1}{\Phi}\left(\frac{VF}{Q} + \Delta v\right) \qquad (1)$$

In this expression Φ is the volume of solution which contains one equivalent of solute, $F$ is equal to 96,500 coulombs, $Q$ is the number of coulombs passed during the time that the boundary sweeps through the volume $V$, $\Delta v$ is a correction term for the change in volume per faraday, at the electrode in the closed side of the apparatus, due to the electrode reaction and to the concentration changes resulting from ionic migration.

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[1] (a) MacInnes and Smith, This Journal, **45**, 2246 (1923). (b) Smith and MacInnes, *ibid.*, **46**, 1398 (1924).

[2] Lewis, *ibid.*, **32**, 862 (1910).

The apparatus, which is shown to scale in Fig. 1, differs only in size, and the relative proportions of its separate parts, from that described in a previous article, so that a further description of its design and manipulation is unnecessary. The calibrated tube C has a length of about 28.5 cm., and an internal diameter of 0.3 cm.; thus it contains a volume ($V$ of Equation 1) of about 2 cc. With a measuring tube of this size the heat generated by the current is conducted away by the thermostat water rapidly enough to prevent an appreciable rise of temperature inside the tube, at least at the current densities employed.

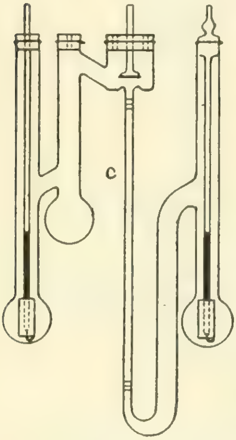

Fig. 1.

The number of coulombs passed ($Q$ of Equation 1) was determined by measuring the time and the current, as described in the first article of this series. Since the current steadily tends to decrease due to the replacing of the measured solution by the less conductive indicator solution, a constantly increasing potential is necessary to keep the current through the apparatus constant. This increasing potential was conveniently obtained by hand operation of the sliding contact of a rheostat across which a battery of small storage cells was connected. (An automatic device for making this adjustment has, however, been developed and will be used in future work.)

As explained in the previous articles, the correct value of a transference number cannot be obtained by the moving-boundary method unless the concentrations of the measured and indicator solutions are adjusted, fairly closely, to the relation

$$C/T = C'/T' \tag{2}$$

in which $C$ and $T$ are the concentrations and the transference number of the solution being measured and $C'$ and $T'$ are the corresponding values for the indicator solution. This means that unless both transference numbers are known in advance it is necessary to make a series of determinations with varying values of the concentration of the indicator solution. Fortunately, the shape of the curve connecting values of the "transference number" thus determined and the concentration of the indicator solution give sufficient indication that adjustment to the condition of Equation 2 has been reached. This is due to the fact that a certain limited amount of adjustment to that condition takes place automatically during the passage of the current.

The substances chosen for investigation were hydrochloric acid and sodium and potassium chlorides, since it was desired to obtain data to test the relation

$$T\Lambda\eta^k = K \tag{3}$$

for chloride ion at 25°. In this expression $T$ is the transference number, $\Lambda$ the equivalent conductance, $\eta$ the relative viscosity, $k$ an empirical constant, and $K$ a constant which, physically interpreted, is the equivalent conductance of an ion constituent in a solution of unit relative viscosity. Equation 3 has been found to hold, at 18°, for a series of chlorides, as has been shown by MacInnes.[3]

## Purification of Materials

The *potassium chloride*, a C. P. (American) product, was recrystallized twice, dried and fused. The *sodium chloride*, also a C. P. (American) product, was further purified by precipitation from a saturated solution, with hydrogen chloride gas, then dried and fused. The *hydrochloric acid* solution was prepared by diluting concentrated C. P. acid to about constant-boiling strength, distilling this solution, and retaining the middle portion of the distillate, which was analyzed gravimetrically for its chloride content. The *lithium chloride* which was used throughout in the indicator solutions, was prepared from a C. P. lithium carbonate of German origin, and pure hydrochloric acid, and the resulting chloride was twice recrystallized.

## The Experimental Results

**Sodium Chloride.**—The results of a series of measurements on solutions of 0.1 $N$ sodium chloride at 25° are given in Table I. A graph of these data is very similar in shape to that shown in Fig. 2, and has a break or flat space between the indicator concentrations 0.069 and 0.081 $N$. The computed "adjusted" concentration, according to Equation 2, is 0.081 $N$. The plot, Fig. 2, is representative of all the results obtained in this investigation in showing a flat space throughout the range of concentrations in which there is adjustment, and a sudden rise and a sudden fall when the concentration is too high and too low, respectively. The average value of the transference number at the concentrations where there is adjustment is 0.3873. The small correction term $\Delta v$ in Equation 1

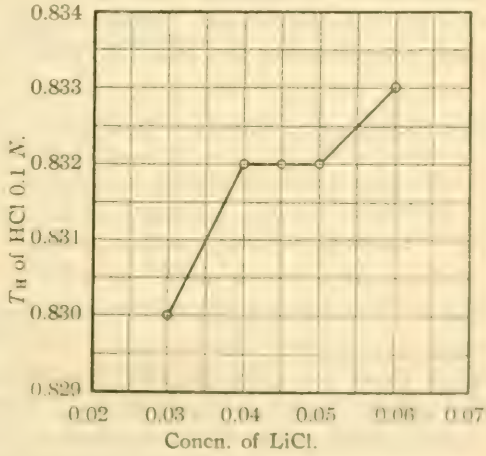

Fig. 2.

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[3] MacInnes, This Journal, **43**, 1217 (1921).

changes this result by —0.0009 making the final value[4] *0.3865*. This constant is particularly interesting since it shows that the values obtained by Jahn and his associates,[5] (0.395 at 18°, and 0.403 at 30°) and on which Noyes and Falk's[6] "best values" are based, are both too high. Hopfgartner's value, 0.383 at 16°, is apparently more nearly correct. That Jahn's values are in error had already been suspected by MacInnes[3] after a study of the values of the transference numbers of other chlorides.

Table I

The Transference Number of Sodium Ion in 0.1 $N$ Sodium Chloride, at 25°

Current 0.01050 amperes

| Concn. LiCl | 0.065 | 0.069 | 0.081 | 0.086 | 0.091 |
|---|---|---|---|---|---|
| Trans. No. $Na^+$ | 0.3859 | 0.3876 | 0.3876 | 0.3905 | 0.3939 |
| | .3865 | .3874 | .3870 | .3903 | .3934 |
| | .3862 | .3872 | .3872 | .3902 | .3932 |

**Hydrochloric Acid.**—Since the "adjustment concentration" of the indicator solution is the concentration at which the leading and following ions at the boundary are moving with equal velocities, it follows that if lithium chloride is used as indicator for a hydrochloric acid solution, the solution of the lithium salt will have to be relatively much more dilute in order that the potential gradient in that solution will increase the velocity of the lithium ions to the required extent. This requirement of equal velocities is the basis of the derivation of Equation 2. Due to this high dilution the lithium chloride indicator solution can be used *over* the hydrochloric acid solution although it is, of course, heavier than the hydrochloric acid at equal concentrations. Measurements made at and near the adjustment concentration are given in Table II, and a plot of the results in Fig. 2. The curve shows that there is complete adjustment throughout the range of indicator concentrations, 0.040 to 0.050, and but small changes when these concentrations are raised and lowered. The correction for the volume change at the electrode is, in this case, negligible. An average value of the number at the adjusted concentrations is *0.8320*. There are no other measurements of this constant at this concentration and tempera-

Table II

The Transference Number of Hydrogen Ion in 0.1 $M$ Hydrochloric Acid, at 25°

Current, 0.0055 amperes

| Concn. LiCl | 0.030 | 0.040 | 0.045 | 0.050 | 0.060 |
|---|---|---|---|---|---|
| Trans. No. $H^+$ | 0.8300 | 0.8321 | 0.8325 | 0.8328 | 0.8338 |
| | .8299 | .8316 | .8322 | .8325 | .8326 |
| | .8298 | .8315 | .8322 | .8319 | .8323 |

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[4] Computations of these corrections are given by Lewis, Ref. 2, and by MacInnes and Smith, Ref. 1 a.

[5] Jahn and others, *Z. physik. Chem.*, **17**, 673 (1901); **58,** 641 (1907).

[6] Noyes and Falk, This Journal, **33,** 1436 (1911).

ture, the nearest being 0.834 at 0.05 *N* and 20° as determined by Noyes and Sammett[7] and the value 0.839 at 0.1 *N* and 18° by Riesenfeld and Reinhold.[8] Denison and Steele's[9] original work gives 0.835 at 0.1 *N* and 18°.

**Potassium Chloride.**—A single determination of the transference number of 0.1 *N* potassium chloride solution was made in the new apparatus using the adjusted concentration of the lithium chloride solution (0.064 *N*) determined in the other investigations of this series, the result being *0.492* for the potassium ion agreeing with the value given by MacInnes and Smith[1] and by MacInnes and Brighton.[10] A series of measurements were also carried out with 0.2 *N* potassium chloride solution, particularly as the number was desired in connection with another investigation carried out in this Laboratory. The results of these measurements are given in Table III. The break in the curve corresponding to Fig. 2, occurs between the lithium chloride concentrations 0.125 and 0.130 *N*, the computed value being 0.125 *N*. The average value of these determinations at the adjusted concentration is 0.4904 but the correction lowers the value to *0.4900*.

TABLE III

THE TRANSFERENCE NUMBER OF POTASSIUM ION IN 0.2 *N* POTASSIUM CHLORIDE, AT 25°

Current, 0.0095 amperes

| Concn. LiCl | 0.110 | 0.125 | 0.130 | 0.150 |
|---|---|---|---|---|
| Trans. No. $K^+$ | 0.4872<br>.4875<br>.4873 | 0.4904<br>.4904<br>.4903 | 0.4905<br>.4906<br>.4904 | 0.4932<br>.4932<br>.4930 |

## Discussion of Results

The apparatus used in this investigation possesses the advantage that correct values of transference numbers are obtained throughout wider ranges of indicator concentrations than with the previous forms. The shape of the curve shown in Fig. 2, which is typical of the results of this investigation, is different from that described in the first paper of this series in that there is no rise to a maximum on the dilute side of the indicator concentrations, and from the curve obtained in the second investigation, with a large apparatus, in that adjustment is not limited to a very narrow range of concentrations.

From the values of the transference numbers and the equivalent conductances, Λ, of the corresponding solutions the conductances of the chloride-ion constituent can be computed for each of the solutions. The results of this computation are given in Table IV.

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[7] Noyes and Sammett, THIS JOURNAL, **24**, 958 (1902).

[8] Riesenfeld and Reinhold, *Z. physik. Chem.*, **68**, 440 (1909).

[9] Denison and Steele, *ibid.*, **57**, 110 (1907).

[10] MacInnes and Brighton, THIS JOURNAL, **47**, 994 (1925).

TABLE IV

CONDUCTANCES OF CHLORIDE ION FROM 0.1 $N$ SOLUTIONS OF DIFFERENT CHLORIDES, AT 25°

| Soln | Equiv. cond. $\Lambda$ | Trans. No. $T_{Cl}$ | $T_{Cl}\Lambda$ |
|---|---|---|---|
| HCl | 390.4 | 0.1680 | 65.58 |
| KCl | 129.0 | .508 | 65.53 |
| NaCl | 106.8 | .6137 | 65.52 |

It will be seen that the product $T_{Cl}\Lambda$ is the same for these solutions, well within the experimental error. The same constancy for this product is shown, at 18°, by these and other chlorides, as has been shown by Lewis[11] and more generally by MacInnes.[3] At the low concentration involved in the experiments described in this paper there is apparently no effect arising from differences in viscosities, which vary by about 1% in the different solutions, although, from analogy from the behavior at 18°, such an effect would be expected.

The results given above show conclusively that at 25° as well as at 18° these chloride solutions have the *same* degree of dissociation. Due to the additivity of the properties of solutions of alkali halides and of the corresponding acids and bases, as well as the failure to discover evidences of an "escaping tendency" of the undissociated solute except at extremely high concentrations, and from similar facts, it has appeared desirable to the authors, and to many others, to consider these solutions as substantially completely dissociated. According to this conception, the variation of the equivalent conductances with the concentration is due to changes of mobilities rather than to changes in the number of ions. A proof that these solutions are *not* completely dissociated would be conclusively furnished by evidence of conduction of the chloride-ion constituent greater, at the corresponding temperature and concentration, than that given for the $T_{Cl}\Lambda$ product in Table IV. So far as has been investigated this product always has the same value at a given concentration and temperature, if allowance is made, at the higher concentrations, for differences in viscosity. The same generalization can be made for the other ions in the range of substances outlined above.[12]

## Summary

The transference numbers of 0.1 $N$ and 0.2 $N$ potassium chloride, 0.1 $N$ sodium chloride solutions and 0.1 $N$ hydrochloric acid have been determined by the moving-boundary method at 25°, with a modified apparatus.

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[11] Lewis, THIS JOURNAL, **34**, 1631 (1912).

[12] Schneider and Braley [THIS JOURNAL, **45**, 1121 (1923)] present what they consider to be ample evidence that these solutions are not completely dissociated, based on transference measurements of mixtures of salt solutions. In a forthcoming paper their conclusions will be discussed on the basis of new measurements.

Using this apparatus, "adjustment" throughout a wider range of indicator concentrations and greater accuracy have been attained.

The product of the chloride-transference number and the corresponding equivalent conductance has been found to be constant for these substances within the experimental error. The bearing of this fact on the theory of the ionization of strong electrolytes is briefly outlined.

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# THE ACTIVITY OF STRONG ELECTROLYTES. IV. THE APPLICATION OF THE DEBYE-HÜCKEL EQUATION TO ALCOHOLIC SOLUTIONS

by

George Scatchard

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# THE ACTIVITY OF STRONG ELECTROLYTES. IV. THE APPLICATION OF THE DEBYE-HÜCKEL EQUATION TO ALCOHOLIC SOLUTIONS

By George Scatchard

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Recently Hückel[1] has published an extension of the Debye theory of the activity of strong electrolytes which, by taking into account not only the magnitudes of the electric charges and the diameters of the ions but also the changing dielectric constant with changing electrolyte concentration, yields an equation that is applicable even in concentrated solutions and goes far toward solving the problems of the activity of strong electrolytes. One very practical advantage of such an equation is that it can be used to extrapolate to zero concentration independently of measurements on very dilute solutions and, therefore, can be applied where such measurements are inaccurate or entirely lacking.

Hückel has tested the equation with electromotive-force measurements on hydrogen, lithium and sodium chlorides in aqueous solution and found agreement with the experimental measurements within a few per cent., even up to 5 $M$ concentrations. So valuable an equation warrants testing in every possible manner. The present paper applies the equation to solutions of hydrogen chloride in alcohol and in alcohol-water mixtures. It comprises the most exacting test yet made of the Debye theory, for the change in the activity coefficient is much greater in alcoholic than in aqueous solutions. In each solvent the agreement with the experimental measurements is within the error of the latter and much better than should be expected from the approximations involved in the derivation of the equation. The extended application also gives evidence bearing on the question of the nature of the action between the ions and the solvent.

## The Debye-Hückel Equation

Hückel develops the general equation for any number of ions of any charge, but for simplicity the formulas of this paper are limited to the special case of a single uni-univalent electrolyte. The constants are given for 25° but the variation with temperature is indicated by inserting the proper power of $T/298.1$. The numerical values of the constants used in this paper, which differ slightly from those of Debye and Hückel, are based on the values of the universal constants used in the "International Critical Tables."

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[1] Hückel, *Physik. Z.*, **26**, 93 (1925).

The equation is[2]

$$-\log f = \frac{A\sqrt{2c}}{1 + \alpha\sqrt{2c}} - B2c \qquad (1)$$

in which $f$ is the ratio of the mean activity of the ions to the mole fraction of either ion ($a_{\pm}/N_{\pm}$) with the convention that the activity approaches the mole fraction at zero concentration, or 0.01 $a_{\pm}/N_{\pm}$ with the convention that the activity approaches the mole percentage at zero concentration, and $c$ is the concentration of the salt in moles per liter, so that $2c$ is the sum of the concentrations of the ions.

For many practical purposes it is more convenient to work with $\gamma$ or $a_{\pm}/m$. Since $\log N_{\pm} = \log m - \log (1 + 0.002\ mw_1) + \log 0.001\ w_1$, then

$$-\log \gamma = -\log f + \log (1 + 0.002\ mw_1) = \frac{A\sqrt{2c}}{1 + \alpha\sqrt{2c}} - B2c + \log (1 + 0.002\ mw_1) \quad (2)$$

in which $w_1$ is the molecular weight, or average molecular weight, of the solvent. The term $\log 0.001\ w_1$ is eliminated through the conventions that both $f$ and $\gamma$ approach unity at zero concentration.

$$A = \frac{249.4}{D_0^{3/2}} \times (298.1/T)^{3/2} \qquad (3)$$

$$\alpha = \frac{2.060 \times 10^8\ a}{D_0^{1/2}} \times (298.1/T)^{1/2} \qquad (4)$$

in which $D_0$ is the dielectric constant of the solvent, and $a$ is the average diameter of the ions (distance of nearest approach of two ion centers) measured in centimeters.

To derive $B$, Hückel assumes that the dielectric constant of the solution is given by the equation $D = D_0 - \delta 2c$, in which $\delta$ is a constant. With this assumption $B$ is not truly a constant, but a rather complicated function of the concentration, whose change, however, is small except when $c$ itself is so small that the effect of the term $B2c$ on the activity coefficient is negligible. For example, calculating $\delta$ from $B$ for 1 $M$ hydrochloric acid, the variation in $f$ or $\gamma$ due to the change in $B$ is never more than 1% up to 1.5 $M$. For most salts the variation is much smaller. For the purposes of the present paper, it is sufficient to know that $B$ varies with $\delta/aD_0^2$.

## Aqueous Hydrochloric Acid

Since Hückel determined the constants for hydrochloric acid from the not very accurate measurements of Ellis, it seems worth while to recalculate them from the more accurate measurements with silver chloride electrodes, and to determine how accurately the formula may be made to fit the experimental data if its application is limited to concentrations not greater than 1 $M$. The values of the constants were determined from the values of

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[2] The constants $A$ and $\alpha$ equal the corresponding constants of my earlier paper [This Journal, **47**, 684 (1925)] multiplied by $1/\sqrt{2}$. $B$ has an entirely different significance.

$\log f'/f''$ for the solution pairs 0.05–0.5 and 0.1–1.0 $M$, these values being taken from the smooth curve of my previous paper.[3] The dielectric constant of water at 25° was taken as 78.8 from the equation of Drude, and the concentrations in moles per liter were determined from the densities to be published in the "International Critical Tables."

The use of Equation 1 or 2 implies the assumption that there is no chemical action between the ions and the water. Constants were also computed on the assumption that the hydrogen ion reacts with one molecule of water in a reaction so nearly complete that the concentration of the unhydrated ion is negligibly small compared to that of the hydrated ion. There does appear to be more direct evidence for the hydration of the hydrogen ion than for that of other ions, and some that only one molecule of water reacts.[4] This computation also serves to illustrate the magnitude of the effect of hydration on the activity coefficient. Such a reaction reduces the total number of moles. Moreover, Equation 1 applies to the activity coefficient of the hydrated ions, while $\gamma$ as determined from the electromotive force is the ratio of the activity of the anhydrous ions to the molality of the sum of anhydrous and hydrated. The equation is

$$-\log \gamma = \frac{A\sqrt{2c}}{1 + \alpha\sqrt{2c}} - B2c + \log\,(1 + 0.001\, mw_1) + 0.5 \log a_w \tag{5}$$

The activity of the water ($a_w$) was determined by graphic integration from that of the acid.

The values found for the constants are given in Table I. Table II contains the values of $\gamma$ calculated by Equation 2 and Equation 5, as well as those derived in the previous paper. It also contains the values of $E_0$ determined by each of the first two series of $\gamma$ values and the smoothed values of the electromotive force by use of the equation

$$E_0 = E + 0.1183 \log \gamma m = E_0' + 0.1183 \log \gamma \tag{6}$$

Equation 2 gives values of $\gamma$ which up to 1 $M$ differ from those previously derived by a nearly constant amount of 0.4%, or 0.2 mv. If $E_0$ be given the value 0.2224 volt instead of 0.2226, the agreement of the actual experimental measurements with the theoretical equation is about the same as with the earlier smooth curve between 0.01 and 1 $M$. The average deviation of Linhart's measurements at lower concentrations is 0.1 mv. instead of zero, and the average deviation of $\gamma$ calculated from the freezing-point measurements of Randall and Vanselow becomes +0.2% instead of —0.1%. Equation 5 also fits the experimental results between 0.01 and 1.0 $M$ almost exactly if $E_0$ be changed to 0.2223 volt. This increases the average deviation of Linhart's measurements on dilute solutions to 0.2 mv., and the average deviation of the $\gamma$ values from freezing points to 0.3%.

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[3] Scatchard, THIS JOURNAL, **47**, 641 (1925).

[4] For example, see Goldschmidt, *Z. physik. Chem.*, **60**, 728 (1907); Fajans, *Naturwissenschaften*, **9**, 734 (1921); Fajans and Joost, *Z. Physik*, **23**, 1 (1924).

TABLE I

CONSTANTS FOR HYDROCHLORIC ACID

| Solvent | $A$ | $\alpha$ | $a \times 10^8$ | $B$ | $2\delta$ |
|---|---|---|---|---|---|
| Water (Eq. 2) | 0.357 | 0.940 | 4.05 | 0.0713 | 26.26 |
| Water (Eq. 5) | .357 | .950 | 4.09 | .0627 | 23.10 |
| 50 mole % alc. | 1.105 | 1.374 | 4.06 | .129 | 13.16 |
| Alcohol | 1.973 | 1.830 | 4.46 | .023 | 1.73 |

TABLE II

MEAN ACTIVITY COEFFICIENTS OF AQUEOUS HYDROCHLORIC ACID

| Molality | $\gamma$ Eq. 2 | $\gamma$ Eq. 5 | $\gamma$ Smooth curve | $E_0$ Eq. 2 | $E_0$ Eq. 5 |
|---|---|---|---|---|---|
| 0.001 | 0.966 | 0.966 | 0.966 | 0.22258 | 0.22257 |
| .002 | .953 | .953 | .954 | 55 | 53 |
| .005 | .930 | .929 | .932 | 49 | 46 |
| .01 | .906 | .905 | .910 | 37 | 33 |
| .02 | .877 | .876 | .881 | 36 | 31 |
| .05 | .832 | .831 | .836 | 37 | 30 |
| .1 | .797 | .795 | .801 | 36 | 27 |
| .2 | .768 | .766 | .774 | 19 | 07 |
| .3 | .758 | .756 | .763 | 26 | 12 |
| .4 | .756 | .754 | .760 | 37 | 22 |
| .5 | .760 | .757 | .763 | 38 | 21 |
| .6 | .767 | .764 | .770 | 39 | 21 |
| .75 | .781 | .778 | .783 | 50 | 31 |
| 1.0 | .814 | .811 | .817 | 37 | 17 |
| 1.5 | .897 | .896 | .905 | 11 | 07 |

Since the theoretical equation involves approximations such that an agreement better than a few tenths of a per cent. is not to be expected, and since neither equation holds so exactly at 1.5 $M$, it seems to me preferable to retain the values of $E_0$ and $\gamma$ previously derived and to attribute the error of 0.4–0.6% to the theory, at least until further work on other substances may indicate a greater precision of the theoretical equations.

It will be noted that the assumption of ionic hydration involves a change of 12% in $B$ and only 1% in $\alpha$. It would be possible to follow Bjerrum[5] and account for all of the second term by assuming that the ions of hydrochloric acid combine with about 8 molecules of water. Measurements on aqueous hydrochloric acid alone appear to offer no evidence as to whether this term should be attributed to change of dielectric constant or to hydration. Evidence will be presented in a later section that one, but only one, molecule of water enters into the reaction.

### Alcoholic Solutions with Varying Acid Concentration

To test the equation with the measurements on alcoholic solutions, $E_0'$ computed from the measurements of Harned and Fleysher[6] at 25° on the cell Pt, $H_2$ | HCl, AgCl | Ag by the equation

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[5] Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

[6] Harned and Fleysher, THIS JOURNAL, **47**, 82 (1925).

$$E_0' = E + 0.1183 \log m \tag{7}$$

was plotted against $\sqrt{2c}$ and a smooth curve drawn through the points. From this curve $\log f'/f''$ was determined for the solution pairs $\sqrt{2c} = 0.4$ and 1.2, 1.2 and 2.2 in alcohol; and 0.4 and 1.0, 1.0 and 2.0 for 50 mole % of alcohol. Since there are no density determinations available on alcoholic hydrochloric acid solutions, the concentrations in moles per liter were calculated by the approximate equation

$$c = \frac{m}{v_0 + km} \tag{8}$$

in which $v_0$ is the specific volume of the solvent, with $k = 0.02$. For aqueous hydrochloric acid, $k$ varies from 0.0182 to 0.0191 between 0.5 and 1.5 $M$. The error in concentration is probably never greater than a few tenths of a per cent. and diminishes rapidly with decreasing concentration.

The dielectric constants of alcohol and of alcohol-water mixtures have been measured by Nernst[7] at about 20°. The values at 25° were calculated by assuming that through this small temperature range the dielectric constant is a linear function of the temperature, and that the fractional change per degree, which is 0.002 for water and 0.004 for alcohol, is a linear function of the mole fraction. The dielectric constants at 25° were plotted against the mole fraction and a smooth curve was drawn through them for interpolation.

The values of the constants for the Debye-Hückel equation are given in Table I. In 50 mole % alcohol the average deviation of the experimental points from the theoretical equation is 0.3 mv. between 0.01 and 2.5 $M$. Below 0.01 $M$ there is a deviation increasing from 1 to 9.5 mv., probably to be ascribed to the difficulties of e.m.f. measurements in very dilute solutions. Since Harned and Fleysher found the average deviation of their points from a smooth curve to be "less than ±0.4 mv." the equation obviously fits the experimental data within the error of the latter. It is impossible to calculate the constants assuming a hydrated hydrogen ion, for there are no means of calculating the activity of the water in these solutions.

In pure alcohol the average deviation is 0.5 mv. between 0.01 and 1.5 $M$. Harned and Fleysher write, "At concentrations up to 0.2 $M$ . . . . the mean variation is less than ±0.5 mv., but for solutions higher than this the consistency is not so great." The point at 3.6 $M$ lies 6.4 mv. off the curve, and the deviations below 0.01 $M$ are about the same as in 50 mole % alcohol.

Danner[8] has measured the electromotive force at 25° of the cell Pt, $H_2$ | HCl, HgCl | Hg in alcohol. Harned and Fleysher note that his results in the range 0.01–0.1 $M$ agree with theirs if the difference between the silver chloride and calomel electrodes be taken as 0.0350 volt, but that his two more concentrated solutions appear to contain small amounts of water. The measurements of Harned and Fleysher in aqueous solution agree with those of Linhart, Noyes and Ellis and Scatchard. Therefore the difference between their silver chloride electrodes and the calomel electrode should be 0.0466 volt, which should be independent of the solvent, since the reaction of the cell Ag | AgCl, HCl, HgCl | Hg is Ag + HgCl(sol.) = Hg + AgCl (sol.). This leaves a discrepancy between the two series of measurements of 11.6 mv., decreasing above 0.1 $M$. From a careful plot of the $E_0$ values of a later section against the mole fraction of water, or better against its square root, it was found that in nearly pure alcohol 0.1 mole % of water corresponds to a change in $E_0$ of 11 or 12 mv. instead of 3 mv. as estimated by Harned and Fleysher. Danner used the most anhydrous alcohol he could prepare; Harned and Fleysher believed that theirs contained less than 0.1 mole % of water. The discrepancies may be fully accounted for if Danner's alcohol be considered 100%,[8a] except above 0.1 $M$ where some water was formed by the action of the acid and alcohol, and Harned and Fleysher's be assumed to be about 99.9 mole %. It is possible that the deviations of their experimental points from the theory below 0.01 $M$ are due to a slightly lower water content.

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[7] Nernst, *Z. physik. Chem.*, **14**, 622 (1894).

[8] Danner, This Journal, **44**, 2832 (1922).

To extrapolate to zero concentration Danner assumed that in dilute solutions $\gamma$ approaches the conductance ratio, $\Lambda/\Lambda_0$; Harned and Fleysher assumed, by analogy to aqueous solutions, that $1 - \gamma = 3(1 - \Lambda/\Lambda_0)/2$. The values of $E_0$ for the cell Pt, $H_2$ | HCl, AgCl | Ag may be calculated from the data given by the authors. Danner's results give —0.0558 volt, or —0.0442 volt corrected for the difference between the two series. Harned and Fleysher's give —0.0552 volt. The Debye-Hückel theory gives —0.0490 volt, which is very near the mean of the other two. In 50 mole % alcohol Harned and Fleysher, through an erroneous interpretation of the Debye theory, extrapolated by assuming that log $\gamma$ is a linear function of $1/D_0$ and found for $E_0$ 0.1479 volt, compared with 0.1530 from the theory.

The values for $a$, the mean diameter of the ions, in water, in 50 mole % alcohol, and in alcohol are found to be 4.05, 4.06 and $4.46 \times 10^{-8}$. The almost exact agreement of the first two should be regarded as a coincidence, and the 10% difference of the third is as small as could be expected. This difference could have been eliminated, however, without greatly changing the agreement with experiment, by subtracting 2 mv. from the value of $E_0$.

The values for $2\delta$, or the change in dielectric constant on the addition of one mole of acid to a liter of solution, are 26.3, 13.2 and 2.7, neglecting the influence of hydration on $B$. But hydration should decrease the first two by about 3.0. Moreover, $\delta$ is too complicated a function for its behavior to be predicted by theory more than approximately. For one-component solvents it should decrease more rapidly than the dielectric constant itself. In mixtures it should be larger than the value calculated from the quantity of water and alcohol in a liter, because the water is attracted to the vicinity of the ions where the effect is largest. Both of these qualitative predictions are fulfilled in this case.

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[8a] Probably it contained a few hundredths of a per cent. of water. The values given apply to this solution rather than to 100.00% alcohol.

## Solutions of Various Concentrations of Alcohol

Harned and Fleysher also measured cells containing 0.1 $M$ hydrochloric acid in 25, 75, 85, 90 and 95 mole % of alcohol, and cells containing 0.01 $M$ acid in the first two. It is possible to calculate $E_0$ from the single measurements by interpolating the values for the constants. Those of $A$ follow from those of $D_0$ alone. Those of $\alpha$ were calculated assuming that $a$ is equal to $4.05 \times 10^{-8}$ throughout. For the interpolation of $B$, $B/D_0^2$ was plotted against the mole fraction, which gave a curve concave upwards, and against weight fraction, which gave one convex upwards. The value used was the mean of the readings from the two curves, which never differed greatly from each other.[9]

TABLE III

HYDROCHLORIC ACID IN ALCOHOL-WATER MIXTURES

| $N_a$ | % | $w_1$ | $v_0$ | $D_0$ | $A$ | $\alpha$ | $B$ | $E_0$ | $E_N$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.00 | 0.0 | 18.02 | 1.0016 | 78.8 | 0.357 | 0.940 | 0.0713 | 0.2226 | 0.2528 |
| .25 | 46.0 | 21.25 | 1.0886 | 49.6 | .715 | 1.185 | .12 | .1882 | .2269 |
| .50 | 71.9 | 25.90 | 1.1643 | 37.1 | 1.105 | 1.374 | .129 | .1530 | .2019 |
| .75 | 88.5 | 33.15 | 1.2231 | 30.2 | 1.505 | 1.518 | .09 | .1004 | .1614 |
| .85 | 93.5 | 37.33 | 1.2439 | 27.9 | 1.695 | 1.580 | .07 | .0687 | .1364 |
| .90 | 95.8 | 39.85 | 1.2540 | 26.9 | 1.790 | 1.609 | .06 | .0485 | .1195 |
| .95 | 98.0 | 42.72 | 1.2641 | 26.0 | 1.884 | 1.636 | .04 | .0198 | .0944 |
| .999 | 99.94 | 46.04 | 1.2738 | 25.2 | 1.973 | 1.830 | .023 | − .0490 | .0295 |

| $N_a$ | $\gamma_0$ | $f_0$ | $\gamma$ 0.01 $M$ | $\gamma$ 0.01 $M$ | $\gamma$ 1.0 $M$ |
|---|---|---|---|---|---|
| 0.00 | 1.00 | 1.00 | 0.906 | 0.797 | 0.814 |
| .25 | 1.95 | 1.66 | .829 | .656 | .670 |
| .50 | 3.88 | 2.69 | .760 | .535 | .479 |
| .75 | 10.8 | 5.92 | .692 | .432 | .295 |
| .85 | 20.0 | 9.64 | .663 | .391 | .234 |
| .90 | 29.6 | 13.4 | .650 | .372 | .205 |
| .95 | 51.8 | 21.8 | .636 | .353 | .177 |
| .999 | 198 | 93.8 | .629 | .351 | .177 |

Table III contains the values of the constants used, the resulting values of $E_0$, and the values of $\gamma$ for 0.01, 0.1 and 1.0 $M$ solutions to illustrate the change of this quantity with changing composition of the solvent.

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[9] This double-graph method lessens the mechanical error of interpolating from three points which do not lie on a straight line and so makes the results easier to duplicate, but it does not, of course, ensure that they are the real values of the function represented.

The values for 99.9% alcohol are those of Table I in which $a \times 10^8 = 4.46$. The $E_0$ values fall on a smooth curve from which $E_0$ may be interpolated for any other concentration. In the 25 and 75 mole % solutions, where $E_0$ was calculated from two different measurements, the difference is 0.5 mv. in each case, or within the error to be expected in the experimental measurements. The averages are given in the table.

The preceding computations have been based on the convention that in each solvent the activity coefficient approaches unity at zero concentration. For the comparison of solutions in different solvents this convention must be dropped. A simple substitute is the retention of the convention for water solutions and the calculation of the activity in an ideally dilute solution in any other solvent relative to that in a solution of the same molality in water. This quantity, which we will call $\gamma_0$, may be defined by the equation

$$0.1183 \log \gamma_0 = E_{0 \text{ in water}} - E_0 \qquad (9)$$

To compare two solutions of finite concentration in different solvents the product $\gamma_0 \times \gamma$ should be used. The two are kept separate because $\gamma$ may be determined more accurately than $\gamma_0$.

By the use of the equations and methods of interpolation given above and of the values given in Table III, it is possible to compute the mean activity of the ions of hydrochloric acid, and therefore other thermodynamic properties, in any mixture of water, alcohol and hydrogen chloride. For solutions less than 1 *M* in acid the accuracy of these calculated values should be about as great as that of the measurements in alcoholic solutions. Up to 2 *M* they should serve as useful approximations.

For theoretical purposes interest attaches to quantities relative to unit number of moles rather than to unit weight. We have used $f$ as the ratio of the activity to the mole percentage with the convention that $f$ approaches unity at zero concentration, and we will define $f_0$ as the activity coefficient of an ideally dilute solution with the convention that $f_0$ is unity for aqueous solutions. Similarly, we will let $E_N$ correspond to $E_0$. These quantities are more precisely defined by the equations

$$E_N = E + 0.1183 \log 0.01\, N_4 f = E_0 + 0.1183 \log 0.1\, w_2 \qquad (10)$$

$$0.1183 \log f_0 = E_{N \text{ in water}} - E_N \qquad (11)$$

## Variation of Activity with Changing Composition of Solvent

Before attempting the important problem of explaining theoretically the variation of $f_0$ with changing composition of the solvent, it will be well to consider the assumptions already made and the further ones necessary for this treatment.

The Debye theory assumes that, in solutions in any given solvent, the activity of an ion is proportional to its mole fraction, except for the effect of the electric charges, through the concentration range in which the theory is applied (Henry's law). For changes from one solvent to another we will assume that for all the solvents considered the factor of proportionality is the same. A generalization of this to all solvents and concentrations leads to the factor unity (Raoult's law). It is highly improbable that this assumption is true generally; it is not for any neutral molecule. The case in which it might be expected to hold best is that of small ions in solvents of high dielectric constant, for there the solvent molecules are attracted so strongly to the ions that the particles may be considered as aggregates of solvent molecules with the ion as core. This is exactly the case of monatomic ions in water or alcohol.

The Debye theory assumes that the energy of the electric charge may be considered to be distributed on the surface of a sphere of radius $b$ and, further, that $b$ is equal to $a$, the mean diameter effective in collisions. If the molecules of the solvent are polarized, the energy of the charge must be distributed over a shell of considerable thickness. The sphere whose surface best represents this distribution must be larger than that influencing collisions but of the same order of magnitude. In the case treated by Debye and Hückel, in which the size of the sphere has only a small effect, it is permissible to make the simplifying assumption that $b$ equals $a$. In the present case the whole effect is due to the size of the ion, and we must discard this much of the assumption. We will make the tentative assumption that $b$ has the same magnitude in all the solvents.

It is assumed that, at least for the alkali and chloride ions, there is no chemical reaction with the solvent—that there is no hydration in the generally accepted sense. For the moment we will make the same assumption regarding the hydrogen ion. It is also assumed that the electrolytes to which the equation applies are completely ionized.

In counting the total number of molecules to compute the mole fraction, it is assumed that the solvent exists entirely as single molecules, or that there is no association in the chemical sense. If there is association but to the same extent in all the solvents there will be no effect on the activity of the ions. Even if the water exists entirely as dihydrol and the alcohol entirely as single molecules, the difference in the $E_N$ values, which is 0.234 volt, will be increased only 0.036 volt. So association cannot change the order of magnitude of the effect, although it may prevent exact agreement of our calculations.

With these assumptions the work, in volt-faradays, of transferring a mole of uni-univalent electrolyte from an ideally dilute solution in a solvent of dielectric constant $D_0'$ to one of the same mole fraction in a solvent of dielectric constant $D_0''$ is

$$E_N' - E_N'' = \frac{14.322 \times 10^{-8}\,(D_0' - D_0'')}{bD_0'\,D_0''} \tag{12}$$

In Fig. 1 the circles are the values of $E_N$ from Table III plotted against the mole fraction of alcohol ($N_a$). The full line AB is the smooth curve through them. The broken line AB is the curve of Equation 12 with $b = 1.65 \times 10^{-8}$ to fit the end-points. Evidently the shape of the two curves is entirely different, and the assumptions given will not account for the phenomenon.

The shape of the curve might be accounted for by assuming that $10^8 \times b$ is equal to about 4 in solutions less than 50 mole % alcohol and then decreases more and more rapidly to 2 in alcohol. It would then be necessary to explain why the size of the ion varies, and no ready explanation offers. Although this does not eliminate variation in $b$ as the true explanation, it does prevent its being a helpful one.

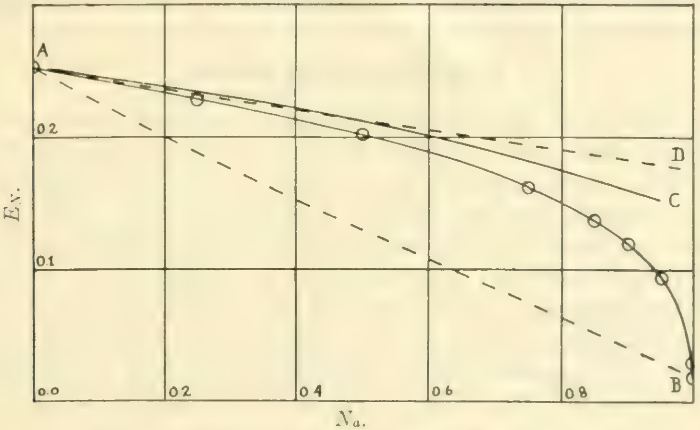

Fig. 1.—Hydrochloric acid in alcohol-water mixtures.

If the hydrogen ion exists in solution not as $H^+$ but as $H_3O^+$, the activity of the water must be taken into account. When the reaction is practically complete, the equation of $f_0$ for $H_3O^+$ and $Cl^-$ is

$$0.1183 \log f_0 = E_{N \text{ for water}} - E_N + 0.05915 \log a_w \tag{13}$$

To calculate $a_w$, the smoothed values of Lewis[10] from the data of Wrewsky[11] were extrapolated to 25°. The values so obtained are only approximate, particularly in solutions rich in alcohol, where the relative error in vapor pressure (which becomes absolute in the logarithm) is large. The full line AC is the curve through the values of $E_N - 0.05915 \log a_w$. Since the assumption of complete hydration is absurd in 100% alcohol, and the curve would there go to infinity, it is not carried beyond 95 mole % alcohol.

The broken line AD is the curve of Equation 12 with $10^8 \times b = 5$, to coincide with AC at 0 and 50 mole % alcohol. At 95 mole % the difference between the two curves is about 30 mv. This difference is somewhat larger than the apparent experimental error in the determination of the curve AC, but it is small considering the very simple assumptions made in calculating the theoretical values. For example, it might be accounted for if, in addition to the electrical effects, the activity coefficient of the $H_3O^+$ ion varies as does that of water, or if $b \times 10^8$ varies from 5 to 4 between 50 and 95 mole % alcohol.

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[10] Lewis, *J. Ind. Eng. Chem.*, **12**, 496 (1920).

[11] Wrewsky, *Z. physik. Chem.*, **81**, 14 (1912).

The evidence against the formation of a still higher hydrate is much stronger. A reaction with two molecules of water would require a very large value of $b$, one with more than two would require negative values. It appears safest to hold merely that the assumption of the existence of the ion $H_3O^+$ fits the experimental data to a better approximation than the assumption of no chemical action, and much better than the assumption of a higher hydrate.

## Alcoholic Solutions of Salts

If the shape of the $E_N$ curve for hydrochloric acid is due to the formation of $H_3O^+$ the effect should be absent from salt solutions. This can be tested by two sets of measurements—the electromotive force of lithium chloride concentration cells, and the solubility of sodium chloride.

Pearce and Hart[12] have measured the electromotive force at 25° of the cell Ag | AgCl, LiCl (0.1 $M$, in water) | Li, Hg | LiCl ($m$, in alcohol), AgCl | Ag through the range 0.006–0.6 $M$ in methyl and ethyl alcohols. The concentrations in moles per liter were calculated by Equation 8 with $k = 0.02$. For aqueous lithium chloride $k$ varies from 0.0180 to 0.0189 from 0.5 to 3.0 $M$. The constants calculated for the Debye-Hückel equation are given in Table IV. Excluding the points of 0.006 and 0.06 $M$ in each series, since they do not lie on a smooth curve through the other points, the average difference between the observed and calculated values of $E$ is 0.6 mv. in ethyl alcohol and 0.9 mv. in methyl alcohol, both probably within the experimental error. Table IV also contains the constants for aqueous lithium chloride determined by Hückel from the data of MacInnes and Beattie.

Table IV

Constants for Lithium Chloride

| Solvent | $D_0$ | $A$ | $\alpha$ | $B$ | $a \times 10^8$ | $b \times 10^8$ | $E_0$ | $E_N$ |
|---|---|---|---|---|---|---|---|---|
| Water | 78.8 | 0.357 | 0.84 | 0.0698 | 3.62 | .. | −0.1305 | −0.1003 |
| Methyl alcohol | 30.2 | 1.505 | 1.62 | .09 | 4.32 | 3.66 | − .2388 | − .1803 |
| Ethyl alcohol | 25.2 | 1.973 | 2.36 | .023 | 5.73 | 4.56 | − .2636 | − .1851 |

The values of $a \times 10^8$ are 3.62 in water, 4.32 in methyl alcohol and 5.73 in ethyl alcohol; those of $b \times 10^8$ are 3.66 from the difference in $E$ for water and methyl alcohol, and 4.56 for water and ethyl alcohol. In each case the $b$ value is intermediate between the $a$ values for the two solutions, and all the $a$ and $b$ values may be considered equal within the error of their determination, so that the change in $E_N$ for lithium chloride is accounted for within the experimental error by the electrical work. Although lithium chloride is generally considered highly hydrated in solution, the reaction with even one molecule of water would require very large values of $b$, and with more than one would require negative values.

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[12] Pearce and Hart, This Journal, **44**, 2411 (1922).

Danner[8] has measured the electromotive force at 25° of the cell Na, Hg (2-phase amalg.) | NaCl (satd. in water), HgCl | Hg, which must be independent of the solvent for saturated solutions. Hückel has calculated the constants for aqueous sodium chloride from the measurements of Allmand and Polack on concentrated solutions, and found $\alpha = 0.545$, $B = 0.0445$, $a = 2.35 \times 10^{-8}$. The average difference between the values of $\gamma$ calculated with these constants and those which I computed from freezing-point and thermal data[2] is 1%; the maximum difference is 3.6% at 0.5 $M$.

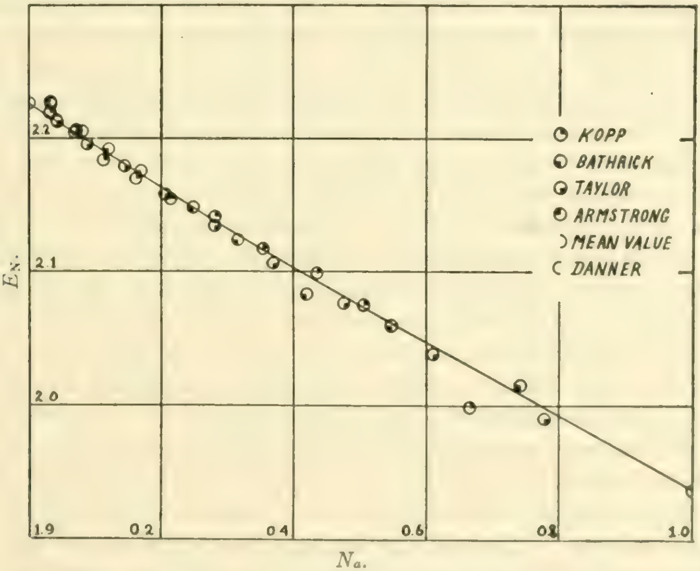

Fig. 2.—Sodium chloride in alcohol-water mixtures.

If it is assumed that $a$ is the same in alcohol and in alcohol-water mixtures as in water, and that the ratio of $B$ for sodium chloride to $B$ for hydrochloric acid is the same in all mixtures of alcohol and water, it is possible to calculate $E_N$ from the solubility of sodium chloride in various mixtures. Again the concentrations in moles per liter were computed by Equation 8 with $k = 0.02$. For aqueous sodium chloride $k$ varies from 0.018 in 0.5 $M$ to 0.021 in 5.0 $M$. The effect of errors in the constants or in the density is very small in solutions rich in alcohol, where the concentration is low. It is doubtful whether these errors are ever larger than those of the solubility measurements. In Fig. 2 are plotted the values of $E_N$ calculated from the solubility measurements of Danner in absolute alcohol, and of Kopp, Bathrick, Taylor and Armstrong in alcohol-water mixtures.[13] For the data of Bathrick and of Taylor, the solubility at 25° was computed by straight-line extrapolation from measurements at 30° and 40°. The curve is that of Equation 12 with $b \times 10^8 = 1.31$; this value was chosen to fit the end-points. The agreement is so very good that it seems advisable to point out that the curve is entirely independent of the measurements on mixtures, but is determined by the measurements in water and alcohol and the dielectric constants of the mixtures.

The change in $E_N$ for sodium chloride is explained quantitatively by the electrical work and there is no possibility of hydration having an important effect. The difference between $E_N$ in water and alcohol is much larger for sodium chloride than for lithium chloride. The reverse should hold if lithium chloride is more hydrated. It will be noted that $b$ for sodium chloride is not much larger than half $a$, for lithium chloride the two are nearly equal, and for hydrochloric acid, assuming the monohydrate, $b$ is equal to or slightly greater than $a$. Variation in this direction is in agreement with the picture of polarization of the solvent molecules by the ions.

From the data, equations and interpolation methods given above, it is possible to compute the activity of the ions of sodium chloride in a solution of any concentration in any mixture of alcohol and water. By successive approximations one could calculate the solubility in any solvent of known dielectric constant. The minimum amount of data necessary for the calculation of the solubility of a salt and the activity of its ions by this method is sufficient activity measurements in one solvent to determine the constants of the Debye-Hückel equation and one measurement of the solubility in another solution of quite different dielectric constant. Great care should be taken, however, regarding both solutes and solvents to which the assumptions underlying Equation 12 are applied. It has already been remarked that monatomic ions in aqueous and alcoholic solutions present the most favorable case. The solubility measurements of Walden[14] show that, in general, solubility is not a function of the dielectric constant alone. In any case, however, Equation 12 should give the norm, the deviation from which is the measure of specific effects.

For potassium chloride the vapor-pressure measurements of Lovelace, Frazer and Sease[15] yield the constants $\alpha = 0.570$, $a = 2.47 \times 10^{-8}$, $B = 0.0235$. These, combined with the solubility measurements,[16] give 1.35 ×

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[13] Kopp, *Ann.*, **40**, 206 (1841). Bathrick, *J. Phys. Chem.*, **1**, 160 (1896). Taylor, *ibid.*, **1**, 724 (1897). Armstrong, *Proc. Roy. Soc.*, **79A**, 568 (1907).

[14] Walden, *Z. physik. Chem.*, **55**, 683 (1906).

[15] Lovelace, Frazer and Sease, THIS JOURNAL, **43**, 102 (1921).

[16] Berkeley, *Phil. Trans.*, **203A**, 207 (1904). Armstrong, *Proc. Roy. Soc.*, **73A**, 568 (1907). de Bruyn, *Rec. trav. chim.*, **11**, 156 (1892). Bathrick, *J. Phys. Chem.*, **1**, 160 (1896). Bodländer, *Z. physik. Chem.*, **7**, 316 (1891).

$10^{-8}$ as the value of $b$. Debye and Mac Aulay[17] found $1.23 \times 10^{-8}$ from freezing-point measurements on mixed aqueous solutions of sucrose and potassium chloride. The agreement is well within the error of their computation.

The $E_N$ curve for potassium chloride is practically identical with that of sodium chloride. It will be noted that in solution dilute in alcohol where hydration is unimportant, the change in $E_N$, and therefore in activity, is much more than twice as great for potassium chloride as for hydrochloric acid. Then the increase in activity of the chloride ion cannot equal that of the potassium ion unless there is an actual decrease in the activity of the hydrogen ion. Such a decrease is extremely improbable; in terms of the theory it represents a negative value for $b$. This also throws some doubt on the validity of the assumption of equal changes in activities for these two ions with changing salt concentration in a single solvent, but there seems to be no direct experimental evidence for or against the assumption in this case.

I take this opportunity to express my gratitude to Professor P. Debye for helpful suggestions and criticism, and to Professor J. A. Beattie for the use of density data before their publication.

## Summary

The Debye-Hückel equation for the activity of the ions of strong electrolytes has been tested by comparison with measurements of the e.m.f. of the cell Pt, $H_2$ | HCl, AgCl | Ag in water, alcohol and 50 mole % alcohol, and is found to fit the data accurately up to at least 1 $M$ in each of these solvents. The relative values of the constants for the different solvents also confirm the theory in a striking manner.

Confirmation of the theory is also found in the e.m.f. measurements on lithium chloride solutions in ethyl and methyl alcohols and water, and in the measurements of the solubility of sodium chloride in mixtures of ethyl alcohol and water.

The variation in the activity of the ions in ideally dilute solutions in different solvents is explained in entirety for sodium and lithium chlorides by the difference in electrical energy. For hydrochloric acid this variation indicates the formation of the ion $H_3O^+$.

It is shown that it is extremely improbable that the change in activity with changing solvent is the same for potassium ion and for chloride ion. It is suggested that the change with changing salt concentration in a single solvent may not be the same for these two ions.

Equations, interpolation methods and data are given which permit the computation of the activity of the ions and other related quantities for hydrochloric acid and sodium chloride in any mixture of alcohol and water.

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[17] Debye and Mac Aulay, *Physik. Z.*, **26**, 22 (1925).

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# CHEMICAL EQUILIBRIA IN NON-IDEAL GASES WHOSE ISOMETRICS ARE LINEAR

by

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# CHEMICAL EQUILIBRIA IN NON-IDEAL GASES WHOSE ISOMETRICS ARE LINEAR

BY FREDERICK G. KEYES

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## Introduction

Until recently there have existed no data whereby any theoretical formulation of chemical equilibria in the case of real gases might be tested. The publication of the experimental results on the ammonia synthesis from the elements by Larson and Dodge[1] and by Larson,[2] therefore, supplies valuable material for comparison with the calculations based on a formulation of actual gas equilibria already some ten years old.

Besides the numerical data pertaining to a given equilibrium, there are required also the fundamental constants of the equation of state for the mixtures of gases entering into the chemical interaction. The studies dealing with the equation of state problem at this Laboratory have established that for a single invariable molecular species, the pressure is a linear function of the temperature as higher temperatures are approached. It is further indicated, on the basis of experimental data soon to be published, that where the curvature of the isometrics can be accurately measured, the departure from linearity is explainable by assuming a quasi-association or aggregation of the single species to double or perhaps higher-order species.[3] In the presentation which is to follow, it will be assumed that single molecular species alone of the reacting gases are present, reserving for a later paper the discussion of the manner in which aggregation of one or more of the reacting gases affects the equilibrium.

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[1] Larson and Dodge, THIS JOURNAL, **45**, 2918 (1923).

[2] Larson, *ibid.*, **46**, 367 (1924).

[3] It is clear that if aggregation is admitted as the reason for the curvature of the isometrics as small volumes and low temperatures are approached, the linearity of the isometrics must logically be viewed as a limiting condition arrived at only as higher temperatures and larger volumes are reached. However, the curvature is so small at relatively small volumes that it is legitimate for many purposes to ignore the curvature of the isometrics.

### The Equation of State of Mixed Gases

The equation of state for a single species under conditions of high temperature and not too small volumes has been shown to be very approximately as follows.

$$p = \frac{RT}{v - \beta e^{-\alpha/v}} - \frac{A}{(v + l)^2} \qquad (1)$$

The existing data pertaining to mixtures are far too meager to enable a definite conclusion to be drawn regarding the form of the equation of state for mixtures. The data available do show, however, that neither Dalton's additive pressure nor Leduc's additive volume propositions are true in general.

The desire to extend the thermodynamic treatment of gaseous reactions to high pressures led several years ago to a systematic experimental investigation of the isometrics of nitrogen-methane mixtures. Non-reactivity, large differences in the individual equation of state constants and convenience of experimental temperature range (0–200°) were factors which determined the choice of these two gases. The complete data obtained by Dr. H. G. Burks are now about ready for publication and the data[4] indicate that mixtures of these two gases follow the form of Equation 1 which represents the individual gases. Moreover, the constants for the mixtures are given within the limits of experimental error by the following equations.

$$\begin{aligned}
A_{\text{mix.}} &= (\sqrt{A}_{CH_4}n_{CH_4} + \sqrt{A}_{N_2}n_{N_2})^2 \\
\beta_{\text{mix.}} &= \beta_{CH_4}n_{CH_4} + \beta_{N_2}n_{N_2} \\
\alpha_{\text{mix.}} &= \alpha_{CH_4}n_{CH_4} + \alpha_{N_2}n_{N_2} \\
l_{\text{mix.}} &= l_{CH_4}n_{CH_4} + l_{N_2}n_{N_2}
\end{aligned} \qquad (2)$$

A generalized equation of state based on this result will be used in the calculation of the increase of the equilibrium constant ($K_p$) of the ammonia synthesis with pressure. The equation is as follows.

$$p = \frac{RT\Sigma n_1}{V - \Sigma n_1\beta_1 e^{\Sigma\alpha_1 n_1/v}} - \frac{(\Sigma n_1\sqrt{A_1})^2}{(V + \Sigma n_1 l_1)^2} \qquad (3)$$

### The Potential Energy of Gases

The potential energy of a gas will be defined as the integral $\int_{\infty}^{v}(\partial U/\partial v)_T dv$, where $U$ is the internal energy of the gas and $v$ the volume. The thermodynamic equation $(\partial U/\partial v)_T = T^2[(\partial P/T)/\partial T]_v$ makes possible the computation of the potential energy, and using Equation 1 there results $-A/(v + l)$. Equation 3, on the other hand, gives

$$-(\Sigma n_1\sqrt{A_1})^2/(V + \Sigma n_1 l_1) \qquad (4)$$

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[4] Burks, *Thesis*, Massachusetts Institute of Technology, **1924**.

The potential energy[5] as obtained through Equation 1 or 3 is a function of the volume alone, aside from the numbers of the different molecular species in the case of a mixture. The departure from linearity of the isometrics, as already stated, has been assumed to be due to a quasi-association or aggregation,[6] an effect which enters appreciably only as lower temperatures are approached, or at high pressures.

## The Specific Heat Capacity of Gases

The specific heat of one component in a mixture of gases has always been assumed to be independent of the presence of the other gases, although the truth of the assumption is not self-evident. Moreover, it is conspicuous that one of the most evident failures of the classical kinetic gas theory is in connection with the accounting it gives of the specific heat capacity of even a pure gas. On the other hand, the general problem of obtaining an adequate theory of the specific heat capacity of gases is of fundamental importance in completing our knowledge of chemical equilibria. Indeed, the present expedient of employing for heat capacities linear or quadratic expansions with temperature necessarily reduces the formulations of equilibria to a semi-empirical procedure, whereby extrapolation is made highly uncertain.[7] In this paper the usual assumption of additivity of heat capacities will be retained.

## The Entropy of an Actual Gas

The general equation for the increment of the entropy is

$$\mathrm{d}S = (\mathrm{d}U + \mathrm{d}W)/T \tag{5}$$

where $U$ is the internal energy and $W$ the reversible work performed by the system. Where $\mathrm{d}W$ is given by $p\mathrm{d}v$, Equation 5 becomes, for a substance of Species 1, where $C_{v_1}$ is the constant-volume heat capacity,

$$\mathrm{d}S = C_{v_1}\frac{\mathrm{d}T}{T} + \left(\frac{\partial p}{\partial T}\right)_v \mathrm{d}v \tag{6}$$

The derivative $(\partial p/\partial T)_v$ may be found from Equation 1. Substituting in Equation 5, and integrating, gives

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[5] Recent attempts to measure the potential energy directly (Joule's experiment) have met with some success in the case of carbon dioxide. See Keyes and Sears, *Proc. Nat. Acad. Sci.*, **2,** 38 (1925).

[6] Keyes, This Journal, **46,** 1584 (1924).

[7] Many formulations of physicochemical problems are based on empirical equations for gaseous heat capacities wherein the actually observed or apparent specific heat data are employed. Evidently in certain instances as, for example, the heat capacities of water, carbon dioxide and hydrogen, a correction should be applied to the observed data to correct for the heat absorbed due to dissociation of the molecule. Moreover, in recent papers attempting to account for the "vibrational specific heat" of hydrogen, "uncorrected" experimental values of the heat capacity of hydrogen have been employed at temperatures approaching 2000°, whereas, according to the existing values for the dissociation of hydrogen, a considerable fraction of the apparent heat capacity is due to heat absorbed by the dissociating molecule.

$$S_1 = \int_0^T C_{v_1}\frac{\mathrm{d}T}{T} + R\int\frac{\mathrm{d}v}{v - \delta_1} + S_1^\circ \qquad (6')$$

where $S_1^\circ$ is the entropy constant for gas number 1. Evidently, since $C_{v_1}$ is not generally known as a function of the temperature, $\int C_{v_1}\mathrm{d}T/T$ cannot be evaluated. The term $R\int \mathrm{d}v/(v - \delta)$ is also given by $R$ log $(v - \delta)$ only as a first approximation.[8]

The change in entropy of a perfect gas, on mixing with other perfect gases, was calculated by Gibbs.[9] Expressed in words, the Gibbs proposition asserts that the entropy of a gas in a mixture at fixed pressure and temperature is the same as it would be if it alone occupied the volume of the mixture. Each of two gases, for example, $n_1$ moles and $n_2$ moles at the same pressure and temperature $p$ and $T$, are contained in compartments of volume $V_1$ and $V_2$ of a container with a removable partition. The equations of state of the two gases, considered perfect, are $V_1 = (RT/p)n_1$ and $V_2 = (RT/p)n_2$. The entropies are, therefore, given by the following (Equation 6) equations, where $S_1^\circ$, $S_2^\circ$ are constants.

$$S_1 = n_1\int C_{v_1}(\mathrm{d}T/T) + R\,n_1 \log V_1/n_1 + n_1S_1^\circ \qquad (7)$$

$$S_2 = n_2\int C_{v_2}(\mathrm{d}T/T) + R\,n_2 \log V_2/n_2 + n_2S_2^\circ \qquad (8)$$

After the partition is withdrawn mixing takes place, the pressure and temperature remaining unaltered. The total volume $V$ containing the two gases is now $V = V_1 + V_2$, and the equation of state of the mixture $V = (RT/p)(n_1 + n_2)$. According to Gibbs' proposition the entropies are

$$S_1' = n_1\int C_{v_1}(\mathrm{d}T/T) + R\,n_1 \log V/n_1 + n_1S_1^\circ \qquad (9)$$

$$S_2' = n_2\int C_{v_2}(\mathrm{d}T/T) + R\,n_2 \log V/n_2 + n_2S_2^\circ \qquad (10)$$

The equations of state of the separate gases and the mixture give the following relations, since $p$ and $T$ are the same before and after mixing: $V_1/n_1 = V_2/n_2 = V/(n_1 + n_2)$ and $V/n_1 = V/(n_1 + n_2)x_1$; $V/n_2 = V/(n_1 + n_2)x_2$, where $x_1$ is $n_1/(n_1 + n_2)$, the mole fraction. Therefore, the difference between Equations 7 and 9, 8 and 10 gives at once $Rn_1$ log $x_1$, $Rn_2$ log $x_2$, which are the magnitudes of the entropy change of mixing.

An actual gas is assumed to have molecules of finite size producing a "volume effect" in the equation of state and a universal attraction, the origin of the cohesive pressure. In Equation 1 the volume effect $\delta$

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[8] The integral $\int \mathrm{d}v/(v - \delta)$ has not been obtained in terms of ordinary functions. As far as required for the present application to the ammonia equilibrium, the approximation is sufficient. It has been found, moreover, that the complete value of the integral differs but little from the approximation until quite small volumes are approached. The complete integral, in fact, differs from $R$ log $(v - \delta)$ by $R\int \mathrm{d}\delta/(v - \delta)$, where $\mathrm{d}\delta = (\alpha\delta/v^3)\mathrm{d}v$. Approximately, the latter integral is of the order of $-\alpha\beta/2v^2$.

[9] Gibbs, Scientific Papers, Longmans, Green and Co., New York, **1906**, vol. I, pp. 156, 165.

is a function of the volume because of the "sponginess"[10] of the molecules and the cohesive pressure contains a constant ($l$) related to a modification in the law of attraction due to the dependence of the molecular polarization on density.

The conception of a perfect gas carries with it the notion of a molecule of such small dimensions that the space for the motion and action of the molecules is the volume of the container. The term $(v - \delta)$, on the other hand, in the case of an actual gas may be taken to represent physically the volume of the gas diminished by the "volume effect" of the molecules and termed the action space ($\Omega$). The term $p + A/(v + l)^2$ represents the sum of the hydrostatic pressure and a pressure (cohesive pressure) acting in the same direction as the hydrostatic pressure. It is proposed to designate this sum by $\pi$.

The equations of the pure gases will now be written $\pi_1\Omega_1 = RT\,n_1$, $\pi_2\Omega_2 = RT\,n_2$, and the mixtures as $\pi\Omega = RT\Sigma n_1$. Thus it is clear that if $\pi$ and $T$ are held constant, $\Omega_1/n_1 = \Omega_2/n_2 = \Omega/\Sigma n_1$. The entropy equation of $n_1$ moles of a single gas may also be written from Equation 6′.

$$S_1 = n_1 \int C_{v_1}(\mathrm{d}T/T) + R\,n_1 \log \Omega_1/n_1 + n_1\,S_1^\circ \tag{11}$$

If it is assumed that a proposition similar to that of Gibbs is true for an actual gas in which $\pi$ and $T$ are maintained the same before and after mixing, the entropy of Gas 1 in the mixture of Gases 1 and 2, for example, will become

$$S_1' = n_1 \int C_{v_1}(\mathrm{d}T/T) + R\,n_1 \log \Omega/n_1 + n_1\,S_1^\circ \tag{12}$$

The difference in entropy is as before, $R\,n_1 \log x_1$, it being understood that $\pi$ and $T$ instead of $p$ and $T$ were maintained the same before and after mixing. The entropy Equations 11 and 12 evidently become identical with Equations 7 and 9, as the volume increases indefinitely and $\pi$ then becomes identical with $p$.

The entropy Equation 11 in generalized form will be used in the computation of the equilibrium equation of an actual gas. The internal energy $U$ may be easily obtained through the equation $U_1 = \int C_{v_1}\,\mathrm{d}T + (\partial U_1/\partial v)_T\mathrm{d}v + U_1^\circ$, in which the second term of the right-hand member is given for a mixture by Equation 4. The two fundamental equations required are, therefore,

$$S = \Sigma n_1 \int C_{v_1}(\mathrm{d}T/T) + R\Sigma n_1 \log \Omega/n_1 + \Sigma n_1\,S_1^\circ \tag{13}$$

$$U = \Sigma n_1 \int C_{v_1}\,\mathrm{d}T - (\Sigma n_1\sqrt{A_1})^2/(V + \Sigma n_1 l_1) + \Sigma n_1\,U_1^\circ \tag{14}$$

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[10] Professor T. W. Richards long ago introduced the idea of atomic compressibility. In the equation of state (1) the $\delta$ term depends on a similar conception in which the distances between the atoms are considered variable and responsive to variations in the intensity of the electromagnetic field, due to the varying density of the molecules produced by changes in volume. The atoms, for the purpose of mathematical simplification in the calculation of $\delta$, were assumed of invariable "size," it being considered that their "hardness" is very likely great in comparison with that of the molecules.

## The Equilibrium Equation

The free-energy equation of Helmholtz will be used because of the form of Equation 1. The equation requires the total energy of the mixture as well as the entropy of the mixture. Equations 13 and 14 may, therefore, be substituted in the free-energy equation $F = U - TS$, giving the following equation.

$$F = \Sigma n_1 \int C_{v1}\,\mathrm{d}T - \frac{(\Sigma n_1 \sqrt{A_1})^2}{(V + \Sigma n_1 l_1)} + \Sigma n_1 U_1{}^\circ - T\Sigma n_1 \int C_{v1} \frac{\mathrm{d}T}{T} - RT\Sigma n_1 \log \frac{\Omega}{n_1} - T\Sigma n_1 S_1{}^\circ \qquad (15)$$

For equilibrium, $\delta\, F_{T,v} = 0$. In carrying out the variation, it is to be noted that the variations $\delta n_1$, $\delta n_2$, etc., are proportional to whole numbers $\nu_1$, $\nu_2$, etc., which are the numerical coefficients in the chemical equation, with respect to which reaction equilibrium is assumed. Equation 15, on rearrangement following the variation operation, becomes

$$\begin{aligned}\Sigma\nu_1 \log x_1 = {} & -\frac{\Sigma\nu_1 U_1{}^\circ}{RT} - \frac{\Sigma\nu_1}{RT}\int C_{v1}\,\mathrm{d}T + \frac{\Sigma\nu_1}{R}\int C_{v1}\frac{\mathrm{d}T}{T} + \frac{2\,\Sigma\nu_1\sqrt{A_1}\,\Sigma n_1\,A_1}{RT(V + \Sigma n_1 l_1)} \\ & - \frac{\Sigma n_1}{\Omega}\,\Sigma\nu_1\beta_1 e^{-\Sigma n_1\alpha_1/V} - \frac{(\Sigma n_1\sqrt{A_1})^2\,\Sigma\nu_1 l_1}{RT(V + \Sigma n_1 l_1)^2} + \frac{\Sigma n_1}{\Omega}\,\Sigma n_1\beta_1 e^{-\Sigma n_1\alpha_1/V}\,\frac{\Sigma\nu_1\alpha_1}{V} \\ & + \frac{\Sigma\nu_1\,S_1{}^\circ - R\Sigma\nu_1}{R} + \Sigma\nu_1 \log\frac{\Omega}{\Sigma n_1} \qquad (16)\end{aligned}$$

Equation 16 at large volume becomes

$$\Sigma\nu_1 \log x_1 = -\frac{\Sigma\nu_1 U_1{}^\circ}{RT} + \Sigma\nu_1 \log\frac{RT}{p} - \frac{\Sigma\nu_1 \int C_{v1}\mathrm{d}T}{RT} + \frac{\Sigma\nu_1 \int C_{v1}\frac{\mathrm{d}T}{T}}{R} + \frac{(\Sigma\nu_1 S_1{}^\circ - \Sigma\nu_1 R)}{R} \qquad (17)$$

which is the usual perfect gas equilibrium equation except for the fact that the specific-heat terms have been retained in the integral form. If $C_{v_1}$, $C_{v_2}$, etc. are constant, $\Sigma\nu_1 \int C_{v_1}\mathrm{d}T/RT$ becomes $\Sigma\nu_1 C_{v_1}/R$, and $(\Sigma\nu_1 \int C_{v_1}\mathrm{d}T/T)/R$ becomes[11] $\Sigma\nu_1 Cv_1/R \log T$, whereupon Equation 17 reduces to

$$\Sigma\nu_1 \log x_1 = -\frac{\Sigma\nu_1 U_1{}^\circ}{RT} + \Sigma\nu_1 \log\frac{RT}{p} + \frac{\Sigma\nu_1 C_{v1}}{R}\log T + \frac{-\Sigma\nu_1 C_{v1} + \Sigma\nu_1 S_1{}^\circ - \Sigma\nu_1 R}{R}$$

It is readily seen from Equation 17, as has been many times pointed out,[12] that a knowledge of the entropy constants and heats of reaction of the reacting gases would enable chemical equilibria to be calculated without actual equilibria data. It is to be emphasized, however, that a knowledge of the $S_1{}^\circ$ constants alone would not be sufficient to formulate correctly a chemical equilibrium in the absence of a knowledge of the correct functional form relating $C_v$ to the temperature.

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[11] The specific heat at constant volume has been used, since for substances whose isometrics are linear in the absolute temperature $C_v$ is a temperature function only, as may be seen at once from the equation $\partial C_v/\partial v = T\partial p^2/\partial T^2$. The constant pressure specific heat, on the other hand, is complicated; $C_p = C_v + R/1 - \alpha\delta/v^2 - 2A/RT\text{-}(v - \delta)^2/(v + l)^3$ from Equation 1.

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 453.

### Application to the Ammonia Equilibrium

The prevailing custom employed to represent equilibrium compositions of a gaseous mixture requires the computation of the quantity $\Sigma\nu_1 \log x_1p$, where $p$ is the total pressure of the equilibrium mixture. This quantity may easily be found from Equation 16 by adding $\Sigma\nu_1 \log p$ to each side of the equation. Operating similarly with respect to Equation 17 and subtracting the latter from the former gives an equation for the logarithm of the ratio of the ordinary equilibrium constants $K_p$ and $K_{p_0}$, where the latter refers to the equilibrium constant as $p$ approaches zero. The general equation becomes

$$\Sigma\nu_1 \log px_1 - \Sigma\nu_1 \log p_0x_1 = \frac{2\Sigma\nu_1\sqrt{A_1}\,\Sigma n_1\sqrt{A_1}}{RT(V + \Sigma n_1l_1)} - \frac{\Sigma n_1}{\Omega}\,\Sigma\nu_1\beta_1e^{-\Sigma n_1\alpha_1/V}$$
$$+ \Sigma\nu_1 \log\frac{p}{\pi} - \frac{(\Sigma n_1\sqrt{A_1})^2\,\Sigma\nu_1l_1}{RT(V + \Sigma n_1l_1)^2} + \frac{\Sigma n_1}{\Omega}\,\Sigma n_1\beta_1e^{-\Sigma n_1\alpha_1/V}\,\frac{\Sigma\nu_1\alpha_1}{V} \qquad (18)$$

The tangent of the log $K_p/K_{p_0}$, $p$ curve as $p$ approaches 0 becomes, from Equation 18,

$$\log K_p/K_{p_0} = \frac{2\Sigma\nu_1\sqrt{A_1}\ \Sigma n_1\sqrt{A_1}}{\Sigma n_1R^2T^2}\,p - \frac{\Sigma\nu_1\beta}{RT}\,p - \frac{\Sigma\nu_1}{(\Sigma n_1)^2}\,\frac{(\Sigma n_1\sqrt{A_1})^2}{R^2T^2}\,p \qquad (19)$$

an equation which is not identical, except for the term involving $\beta$, with a special equation obtained by Gillespie[13] through considerations leading from the fugacity rule of Lewis and Randall.[14] This is to be expected, however, since the treatment employed to obtain Gillespie's equation depends, among other things, on assuming the additivity of volumes of the gases composing the equilibrium mixtures, whereas Equation 19 is a special equation obtained by combining the constants of the individual gases according to Equations 2 above, giving Equation 3.

It may be pointed out that although the pressure of a gaseous mixture at very large volumes ought to be given approximately by assuming either additive volumes or additive constants, nevertheless, the form of the resulting mass-action laws at low pressures is not the same.

The constants of the gases pertaining to the ammonia synthesis are given in Table I together with the other quantities required in computing the quantity $K_p/K_{p_0}$. Argon is included because of its presence in the equilibrium mixture used by Larson and by Larson and Dodge.

The constants for hydrogen and nitrogen are substantially the same that Gillespie has used to compute the $K_p/K_{p_0}$ ratio. The constants for ammonia are, however, different and depend on recent and extensive $p$-$v$-$T$ data for ammonia obtained by Lawrence.[15] The ammonia molecule

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[13] Gillespie, This Journal, **48**, 28 (1926).

[14] Ref. 12, p. 226.

[15] Lawrence, *Thesis*, Massachusetts Institute of Technology, **1924**.

TABLE I

CONSTANTS FOR THE GAS IN THE REACTION $^3/_2H_2 + {}^1/_2N_2 = NH_3$

| | | | |
|---|---|---|---|
| $A_{H_2} = 0.159 \times 10^6$ | $\sqrt{A_{H_2}} = 0.3987 \times 10^3$ | $\beta_{H_2} = 19.4$ | $\alpha_{H_2} = 5.9$ |
| $A_{N_2} = 1.288 \times 10^6$ | $\sqrt{A_{N_2}} = 1.135 \times 10^3$ | $\beta_{N_2} = 49.5$ | $\alpha_{N_2} = 30.3$ |
| $A_{NH_3} = 5.68 \times 10^6$ | $\sqrt{A_{NH_3}} = 2.383 \times 10^3$ | $\beta_{NH_3} = 81.4$ | $\alpha_{NH_3} = 110.1$ |
| $A_A = 1.58 \times 10^6$ | $\sqrt{A_A} = 1.257 \times 10^3$ | $\beta_A = 51.0$ | $\alpha_A = 0$ |
| $l_{H_2} = -2.4$ | $\Sigma\nu_1\sqrt{A_1} = 1217.4$ | $R = 82.06$ cc. 'atm. 'mole | |
| $l_{N_2} = 6.2$ | $\Sigma\nu_1\beta_1 = 27.55$ | | |
| $l_{NH_3} = 31.5$ | $\Sigma\nu_1\alpha_1 = 86.1$ | | |
| $l_A = -10.0$ | $\Sigma\nu_1 l_1 = 32.0$ | | |

possesses, like the water molecule, a natural or permanent electric moment in distinction from the hydrogen or nitrogen molecule which possess no permanent moments. The aggregation effect is relatively large in consequence for ammonia, and the constants in Table I were obtained after "correcting" the isometrics for curvature. As a matter of fact, when the curvature of the isometrics is neglected, the $A$ and $\beta$ values both are large as compared with those obtained from the more nearly linear isometrics at high temperatures where Equation 1 applies with great exactness.

From Equation 18 there results the following equation for the ammonia equilibrium, using the constants from Table I.

$$\log_{10} K_p/K_{p0} = 12.886\,\frac{\Sigma n_1\sqrt{A_1}}{T(V + \Sigma n_1 l_1)} - 11.965\,\frac{\Sigma n_1}{\Omega}\,e^{-\Sigma n_1\alpha_1/V} + \log_{10}\pi/p - 0.16936\,\frac{\Sigma(n_1/A_1)^2}{T(V + \Sigma n_1 l_1)^2} + 37.393\,\frac{\Sigma n_1}{\Omega V}\,\Sigma n_1\beta_1 e^{-\Sigma n_1\alpha_1/V} \qquad (20)$$

By means of this equation the numbers in the last column of Table II

TABLE II

AMMONIA EQUILIBRIUM DATA OBSERVED AND CALCULATED FROM EQUATION 20

| $t$, °C. | $p$, atm. | $NH_3$, % | $n_{H_2}$ | $n_{N_2}$ | $n_{NH_3}$ | $\Sigma n_1$ | G. L. P. $K_p/K_{p0}$ obs. | G. H. P. $K_p/K_{p0}$ obs. | $K_p/K_{p0}$ calcd. |
|---|---|---|---|---|---|---|---|---|---|
| 375 | 50 | 19.44 | 1.1018 | 0.3268 | 0.3463 | 1.7814 | 1.0500 | | 1.030 |
| | 100 | 30.95 | 0.8669 | .2486 | .5029 | 1.6248 | 1.1400 | | 1.096 |
| 450 | 50 | 9.17 | 1.3532 | .4106 | .1787 | 1.9489 | 1.041 | | 1.011 |
| | 100 | 16.35 | 1.1728 | .3505 | .2990 | 1.8287 | 1.095 | | 1.039 |
| | 300 | 35.50 | 0.7851 | .2213 | .5574 | 1.5702 | 1.344[a] | 1.537 | 1.283 |
| | 600 | 53.60 | .5076 | .1289 | .7425 | 1.3854 | 1.993[a] | 2.280 | 2.097 |
| | 1000 | 69.40 | .3138 | .0642 | .8717 | 1.2560 | 3.705[a] | 4.238 | 5.889 |
| 475 | 50 | 7.13 | 1.4089 | .4292 | .1416 | 1.9861 | 1.029 | | 1.008 |
| | 100 | 12.98 | 1.2546 | .3778 | .2444 | 1.8832 | 1.068 | | 1.028 |
| | 300 | 31.00 | 0.8660 | .2482 | .5035 | 1.6242 | 1.358[a] | 1.472 | 1.227 |
| | 600 | 47.50 | .5935 | .1574 | .6852 | 1.4425 | 1.819[a] | 1.972 | 1.858 |
| | 1000 | 63.50 | .3817 | .0868 | .8264 | 1.3013 | 3.106[a] | 3.366 | 4.113 |
| 500 | 50 | 5.58 | 1.4526 | .4438 | .1125 | 2.0152 | 1.028 | | 1.005 |
| | 100 | 10.40 | 1.3207 | .3998 | .2004 | 1.9273 | 1.053 | | 1.021 |
| | 300 | 26.20 | 0.9587 | .2791 | .4417 | 1.6859 | 1.310[a] | 1.349 | 1.177 |
| | 600 | 42.10 | 0.6757 | .1848 | .6304 | 1.4973 | 1.724[a] | 1.777 | 1.688 |

[a] Extrapolated.

were computed, using for the "$n$" values computed from the equilibrium data of Larson and Dodge, and of Larson. The formulas used to compute the number of moles are given below where $a$ is the percentage of ammonia formed from the original gaseous mixture containing 0.3% of argon, 76.2% of hydrogen and 23.5% of nitrogen. Moles of ammonia $= 2.1277\ 100/(100 + a) = y$; moles of hydrogen $= 0.12127 + {}^3/_2\,(1 - y)$; moles of nitrogen $= {}^1/_2\,(1 - y)$; moles of argon $= 0.0064$; total moles $= 2.1277\ 100/(100 + a)$.

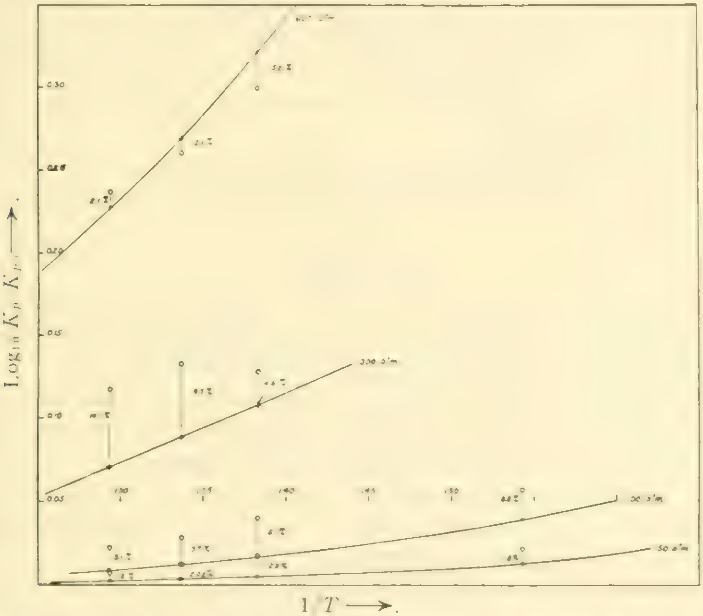

Fig. 1.—The ammonia equilibrium experimental results of Larson and Dodge, and of Larson, - - - ○; computed values from Equation 20, —— +.

Table II contains for comparison also the $K_p/K_p$ ratio computed from the equations given by Gillespie,[16] which represent the first series (Larson and Dodge) of measurements of the equilibrium to 100 atm. and the second series (Larson) to 1000 atm. There is a discontinuity between the two series and for this reason two columns are given in Table II headed G. L. P. and G. H. P., referring to Gillespie's equations representing the low-pressure data and the high-pressure data. The low-pressure equation has been used to extrapolate to the three higher pressures for comparison purposes. In general, the computed ratios at 50, 100 and 300 atm. are lower than those observed, while at 600 atm. the computed ratios lie between the two "observed" ratios at the two temperatures

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[16] Gillespie, *J. Math. Phys., Mass. Inst. Techn.*, **4**, 84 (1925).

450 and 475°. The 1000-atm. ratios, however, are much larger than the observed. It is of interest to observe that at higher pressures the equilibrium-constant ratio shows a large variation with a comparatively small change in the equilibrium composition. For example, at 450° and 1000 atm. an increase in the percentage of ammonia from 68.4 to 71.0 changes the ratio from 4.24 to 4.85. Including the 100-atm. pressure range, the calculated and observed ratios are in accord within 5%, while in the high-pressure range the ratios are in agreement as regards order of magnitude. The percentage of ammonia deduced from the calculated ratios is not, however, greatly different from the observed amounts of ammonia at 300, 600 and 1000 atm. Fig. 1 exhibits the logarithm of the computed ratios for constant pressures plotted against the reciprocal of the absolute temperature.

The tedious computations necessary to secure the material for Table II were made by Miss Charlotte T. Perry, for whose assistance the writer is deeply grateful.

## Summary

1. A generalized equation of state for mixtures is given applicable to gases whose isometrics are linear. This equation is based on experimental results obtained for binary mixtures of nitrogen and methane.

2. An equation for the entropy of a gaseous mixture is given which becomes identical with the familiar entropy equation for perfect gases at low pressures. By means of the entropy equation and the energy equation, a general expression for the equilibrium constant ($K_p$) is deduced by using the thermodynamic function $F = U - TS$, the free energy for temperature and volume as independant variables.

3. Comparison of the $K_p/K_{p_0}$ equation (ratio of $K_p$ at $p$ atm. to $K_{p_0}$ at zero pressure) with the experimental results of Larson and Dodge and of Larson for the ammonia synthesis indicates tolerable agreement to 600 atm. The computed results ($K_p/K_{p_0}$) are lower than the experimental results by several per cent. to 100 atm. The calculated ratios ($K_p/K_{p_0}$) at the three temperatures for which equilibrium measurements exist at high pressures (Larson) are in agreement as regards order of magnitude, the ratios observed and calculated being as follows.

| $t$, °C. | | 300 atm. | 600 atm. | 1000 atm. |
|---|---|---|---|---|
| 450, | obs. | 1.537 | 2.280 | 4.238 |
| | calcd. | 1.283 | 2.097 | 5.889 |
| 475, | obs. | 1.472 | 1.972 | 3.366 |
| | calcd. | 1.227 | 1.858 | 4.113 |
| 500, | obs. | 1.349 | 1.777 | |
| | calcd. | 1.177 | 1.688 | |

4. Experimentally, log $K_p/K_{p_0}$ is practically linear in $1/T$. This cannot be strictly true for the computed values of log $K_p/K_{p_0}$ (Equation

20); nevertheless, numerically the linear relation does hold rather closely over temperature range 375 to 500° (Fig. 1).

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# THE TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM CHLORIDES AND OF THEIR MIXTURES

by

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# THE TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM CHLORIDES AND OF THEIR MIXTURES

By Jane Dewey

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The paper[1] just preceding this contains a discussion of the experimental results and conclusions of Schneider and Braley[2a] and of Braley and Hall,[2b] relative to the question of the presence or absence of ionic complexes in aqueous solutions of potassium and sodium chlorides. It is shown in that paper that their results are in accord with the assumption of simple ions only, within their experimental error, with the possible exception of some of the measurements in which the sum of the concentrations of the two salts is 0.2 $N$, and the proportion of sodium chloride small. In that region, according to the measurements of the first mentioned authors, the transference number of the sodium ion drops nearly to zero. This could be accounted for by the presence of complex negative ions, containing sodium, which carry as much of this element when moving under the influence of the current as the positively charged ion moving in its normal direction. Their results, if verified, would make some such assumption necessary. On account of the importance of the subject, and since none of the more recent ideas on ionization are tenable if such complexes are present in solutions, it has seemed desirable to repeat the experiments at the concentration mentioned. In addition, the transference numbers of the pure salts have been found at the same concentration, since without them the results of measurements on mixtures cannot be interpreted. A change in the method of analysis of the mixtures resulting from the electrolysis was also made.

## The Transference Measurements

The transference apparatus described by Washburn[3] was used except that no stopcock was placed on the cathode side. The cathode was made by winding a piece of platinum gauze, about 10 cm. long and 1 cm. wide, into a coil just small enough to slip into the apparatus. This coil was heavily silver plated, and covered with an adherent coating of silver chloride by alternate chloridizing and reducing electrolytically. The anode was a spindle consisting of 3 meters of 1.2mm. silver wire formed in the manner described by Washburn. No chloride separated from either electrode, or entered into colloidal solution, and it was not found necessary to filter the electrode portions after the passage of the current. During a determination about 20 milliamperes was passed through the apparatus for 16 hours, using a potential of 16 v.

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[1] MacInnes, This Journal, **47**, 1922 (1925).

[2] (a) Schneider and Braley, *ibid.*, **45**, 1121 (1923). (b) Braley and Hall, *ibid.*, **42**, 1770 (1920).

[3] Washburn, *ibid.*, **31**, 322 (1909).

Instead of analyzing the middle portions chemically, measurements of their conductivity were made and the conductivities found were compared with that of the original solution. The maximum change observed was less than 0.1%, and was usually nearly zero. The electrode portions were always tested for alkalinity and if any was found the run was discarded.

Two silver coulometers of the Richards type with the anodes surrounded by alundum crucibles were used, one being connected in series at each terminal of the transference apparatus.

The transference measurements were made in a thermostat at 25° ± 0.1°.

## The Conductivity Measurements

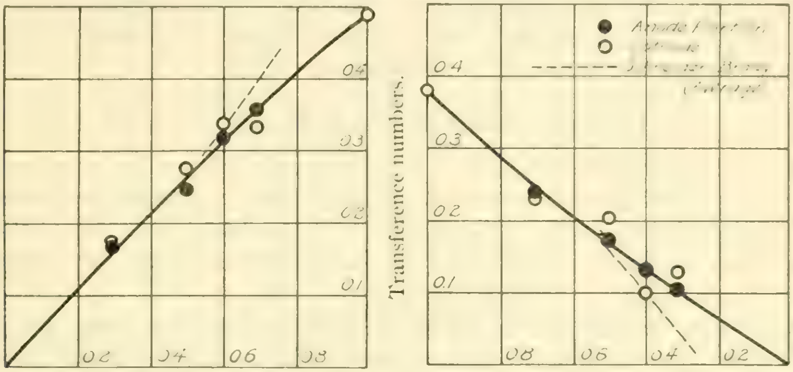
Conductivity measurements were used, in a manner to be described below, to analyze the solutions resulting from the transference determinations on salt mixtures, as well as for testing the constancy of the middle portions. An "extended wire" bridge with a total resistance of 233 ohms., of which one-tenth was due to the slide wire, was used, in connection with a Curtis resistance box, and a tuning-fork oscillator as a source of current. The capacity of the cell was balanced by the use of a large variable condenser. The conductance cell was of the pipet type, with electrodes 1 cm. in diameter and 8 cm. apart. As a thermostat for the conductance measurements a Dewar tube containing cracked ice in distilled water was used. With this apparatus a precision of 0.005% could be readily obtained.

## Preparation of Materials

Potassium chloride from a well-known German firm was recrystallized and fused before using. C. P. Sodium chloride of American manufacture was recrystallized twice by precipitation with hydrogen chloride and then fused. The water was redistilled from alkaline permanganate solution in a tin-lined still and stored in resistance-glass bottles.

## Experimental Results

**The Transference Numbers of the Pure Salts.**—Since the transference numbers of the pure salts enter into the computation of the transference numbers of the mixtures (see Equation 2 of the preceding paper), measurements of the values of these constants for potassium and sodium chlorides at 0.2 $N$ were first made. A large amount of effort was expended in this part of the research, since the results obtained for the transference number of the potassium ion in potassium chloride solution were consistently lower than those obtained by the moving-boundary method, with which measurements were simultaneously being made in this Laboratory.[4] The results are also considerably lower than those found by German investigators and summarized in a paper by Noyes and Falk.[5] The average result for the transference number of the potassium ion in 0.2 $N$ potassium chloride as determined in this research is 0.486, and that by the moving-boundary method 0.490. Many attempts were made to find the reason for this difference, all without success, the Hittorf method always yielding the same result in spite of changes in the design and nature of the electrodes, etc. The results are summarized in Table I, which is self-



Ratio—moles of KCl: total concn. Ratio—moles of NaCl: total concn.

Fig. 1.—The transference numbers of mixtures of potassium and sodium chlorides, at 0.2 $N$.

TABLE I

THE TRANSFERENCE NUMBER OF POTASSIUM ION IN 0.2 WEIGHT NORMAL POTASSIUM CHLORIDE AT 25°

| Wt of silver deposited | Change in chloride content Millimoles Anode portion | Cathode portion | Transference number $T_K$ Anode | Cathode |
|---|---|---|---|---|
| 0.7648 | 3.438 | 3.424 | 0.4850 | 0.4830 (a) |
| 1.4203 | 6.390 | 6.397 | .4854 | .4859 (a) |
| 1.7529 | 7.926 | 7.915 | .4878 | .4871 (b) |
| 1.0650 | 4.790 | 4.789 | .4852 | .4851 (c) |
| 0.7393 | 3.543 | ... | .4835 | ... (d) |

(a) Silver plated platinum anode and cathode. (b) Silver wire anode. (c) Run in air. (d) Zinc anode. Av., omitting (d) 0.4856 ± 0.0005.

THE TRANSFERENCE NUMBER OF SODIUM ION IN 0.2 WEIGHT NORMAL SODIUM CHLORIDE AT 25°

| | | | | |
|---|---|---|---|---|
| 1.0504 | 3.671 | 3.686 | 0.3786 | 0.3771 |
| 0.9685 | 3.370 | 3.358 | .3762 | .3748 |
| | | | Av. 0.3767 ± 0.0006 | |

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[4] See Smith and MacInnes, THIS JOURNAL, 47, 994 and MacInnes and Brighton, *ibid.*, 47, 1009 (1925).

[5] Noyes and Falk, *ibid.*, 33, 1436 (1911).

explanatory. One determination was made in the air instead of in a thermostat to test for possible leaks, and another was made with a zinc anode to repeat the practice of the German experimenters. The results by the two latter procedures are, however, slightly lower than the others. The difference, about 0.8%, between the results of the Hittorf and the moving-boundary methods makes no difference in the conclusions of this paper, being of imperceptible magnitude on a plot of the scale of Fig. 1. The difference will, however, be investigated further.

## The Transference Numbers of the Salt Mixtures

In the determinations of the transference numbers for the solutions of mixtures of sodium and potassium chlorides, the electrolyses were carried out as for the pure salts. The analysis of the resulting electrode portions was, however, more complicated. After these portions had been collected and weighed, check determinations were made of their conductances, after which the amount of chloride-ion constituent was found by precipitation and weighing as silver chloride. These latter data yielded the total number of moles of salt in the portion under consideration. With this information and with a knowledge of the manner in which the conductance of the solutions changes with the concentration and the proportion of each salt present, this proportion could be found with precision. The computation, however, required the use of a short series of approximations. The fact that the conductivity at any one total concentration varies, for this pair of salts, with the fraction $x$ of potassium chloride in a manner very close to linear greatly facilitated the computations. The data for the conductances of the mixtures of the salts are given in Table II, in which it can be seen that the maximum deviation from linearity is about 0.3% at 0.2 $N$ and 0.4% at 0.25 $N$. A single measurement was also made at 0.1 $N$ with a fraction $x$ of 0.5 and the deviation was found to be 0.00%. For any intermediate concentration this deviation from the law of mixtures can be interpolated with all the accuracy necessary. The changes of the conductances of the pure salts at 0° for the range of concentrations involved in this research are given in Table III.

The actual computation was carried out as follows. From the weight of the sample of electrode portion, corrected to vacuum, was subtracted the approximate weight of salt in the portion. The total salt concentration of the sample was then calculated from the weight of the water found in this way and from the weight of the silver chloride found in the analysis. The conductances of pure potassium chloride and of pure sodium chloride at this concentration were then interpolated exactly from the data contained in Table III. The fraction $x$ of potassium-ion constituent in the sample was then calculated on the basis of a linear relation between this fraction and the conductance. This gave the necessary data to compute a new, and very close to exact, value of the weight of salt in the sample and of the total salt concentration. The calculation of the fraction $x$ was then repeated, taking account of the deviation of the conductance values from the linear relation at the given concentration. This process could, of course, be continued until repetitions yielded the same values. Then, having the total concentration and the proportion of each salt in the solution the calculation of the transference numbers was continued in the usual way.

Table II

Equivalent Conductances of Mixtures of Sodium and Potassium Chlorides at 0°

Total Concentration 0.2000 Weight Normal

| $x$ | $\Lambda$ observed | $\Lambda$ calculated | $\Delta$ |
|---|---|---|---|
| 0.00 | 54.639 | .... | ..... |
| .25 | 58.265 | 58.294 | −0.029 |
| .50 | 61.908 | 61.949 | − .041 |
| .75 | 65.572 | 65.603 | − .031 |
| 1.00 | 69.258 | .... | ..... |

Total Concentration 0.2500 Weight Normal

| $x$ | $\Lambda$ observed | $\Lambda$ calculated | $\Delta$ |
|---|---|---|---|
| 0.00 | 53.725 | .... | ..... |
| .25 | 57.282 | 57.323 | −0.041 |
| .50 | 60.858 | 60.921 | − .063 |
| .75 | 64.480 | 64.520 | − .040 |
| 1.00 | 68.118 | .... | ..... |

Table III

Specific Conductances of Potassium and Sodium Chlorides at 0°

| | Concn., moles per 1000 g. of water | | | | |
|---|---|---|---|---|---|
| | 0.15 | 0.16 | 0.17 | 0.18 | 0.19 |
| Sp. conductance, KCl | .010481 | .011144 | .011803 | .012460 | .013115 |
| NaCl | .0083685 | .0088860 | .0094037 | .009911 | .010422 |

| | Concn., moles per 1000 g. of water | | | | | |
|---|---|---|---|---|---|---|
| | 0.20 | 0.21 | 0.22 | 0.23 | 0.24 | 0.25 |
| Sp. conductance, KCl | .013852 | .014419 | .015078 | .015731 | .016380 | .017030 |
| NaCl | .010928 | .011430 | .011933 | .012435 | .012937 | .013431 |

Table IV

Transference Numbers of 0.2 Weight Normal Mixtures of Potassium and Sodium Chloride at 25°

| Portion | Mole ratio KCl | Silver deposited G. | Size of portion G. of water | Transference numbers $T_K$ | $T_{Na}$ |
|---|---|---|---|---|---|
| Anode | 0.2960 | 1.0122 | 107.56 | 0.174 | 0.239 |
| Cathode | .2960 | .... | 82.80 | .178 | .229 |
| Anode | .4988 | 1.2037 | 97.18 | .275 | .172 |
| Cathode | .4988 | .... | 83.75 | .247 | .203 |
| Anode | .6002 | 1.1702 | 103.19 | .316 | .131 |
| Cathode | .6002 | .... | 84.01 | .339 | .097 |
| Anode | .6936 | 1.0013 | 108.14 | .357 | .105 |
| Cathode | .6936 | .... | 81.77 | .332 | .127 |

The results of the experiments on the transference numbers of the ions in the solutions of the mixtures of the two salts are given in Table IV, which is self-explanatory, and are plotted in Fig. 1. In the figure it can be seen that the results from the anode portions are accurately represented by the theoretical line. The results from the cathode portions were subject to a greater error from some unknown cause, but the points are scattered uniformly about the theoretical curve. Some measurements were also made with a still smaller proportion of sodium chloride than those shown in the table, but were not successful. They at least, however, showed movement of sodium-ion constituent in a region of concentrations in which the results of Schneider and Braley would lead one to expect no such movement. It is hoped to continue this research with somewhat changed experimental arrangements, although these experiments, together with the considerations outlined in the preceding article, appear to be ample to decide the matter under discussion.

## Conclusion

The results of Schneider and Braley on the transference numbers of sodium- and potassium-ion constituents in a mixture of the chlorides at a total concentration of 0.2 $N$ have been repeated, with a modified experimental technique. Their experiments indicated that with a low proportion of sodium chloride the transference number of the sodium-ion constituent drops nearly to zero, a result which has not been confirmed by the experiments described in this paper. Since the new results follow closely the prediction based on the assumption of simple ions, and no ionic complexes, the conclusion of Schneider and Braley that such complexes are present in these solutions is also not confirmed.

Cambridge, Massachusetts

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# PUBLICATIONS

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# Electromotive-Force Measurements in Aqueous Solutions of Hydrochloric Acid Containing Sucrose

by

George Scatchard

[Reprint from the Journal of the American Chemical Society, **48**, 2026 (1926).]

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 174]

# ELECTROMOTIVE-FORCE MEASUREMENTS IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID CONTAINING SUCROSE[1]

BY GEORGE SCATCHARD

RECEIVED MARCH 4, 1926 PUBLISHED AUGUST 5, 1926

Solutions of sucrose in water have long occupied a prominent position in the study of the properties of solutions, and particularly in the study of reaction rates. With the correlation of reaction rates with activities, electromotive-force measurements in solutions containing sucrose have become important. All the measurements so far reported, however, have been made in cells containing liquid junctions, and with those junctions made by dipping a small tube containing the lighter liquid into a larger one containing the heavier. Most of them have been made with a hydrogen electrode.

This paper describes an attempt to study the problem in more detail by dividing it into two parts: a study of the effect of sucrose on the liquid-junction potential between hydrochloric acid and saturated potassium chloride, and a study of the effect of sucrose on the potential of the hydrogen electrode. The measurements do not agree with those in the literature, and they disclose three sources of errors which probably account for the discrepancies. They give a more precise knowledge of the ion activities in sucrose solutions, and they comprise the first experimental study, so far as I am aware, of the effect of a non-electrolyte solute on liquid-junction potentials.

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[1] Reported to the Physical-Inorganic Division of the American Chemical Society at Los Angeles, August 7, 1925. The experimental work was carried out in 1924 during the tenure of a National Research Fellowship.

## Cells with Liquid Junctions

The electromotive force at 25° of the cell Hg | HgCl, KCl (satd.) | HCl ($c_1$), sucrose ($c_2$), AgCl | Ag was measured in the flowing-junction apparatus previously described,[2] which gives a continuously renewed junction of large cross section but of almost knife-edge thinness, and which also permits a study of the effect on the liquid-junction potential of interdiffusion of the two solutions without the disturbance of turbulent mixing. The concentration of hydrochloric acid was kept constant at 0.1012 mole per liter, while that of sucrose was varied from zero to 700 g. per liter. All weights are reduced to vacuum.

The sucrose had been precipitated with alcohol, dried in a vacuum at 50°, and then in a current of dry air at the same temperature.[3] The other materials were all prepared as for the earlier studies.[2,4] The silver chloride electrodes were all prepared in the solution without sucrose and then washed several times in the solution in which they were to be used. Only two measurements, with a single filling of the apparatus, were made with each solution. Otherwise the procedure was the same as that described in the papers cited.

Table I

Electromotive Force of the Cell Hg | HgCl, KCl (satd.) | HCl (0.1012 *N*), sucrose, AgCl | Ag

| Sucrose, g. per liter | *E* flowing | Dev. from mean | *E* maximum | Dev. from mean |
|---|---|---|---|---|
| 0.00 | 0.0431 | $0.0000_6$ | .... | .... |
| .00 | .0431 | $.0000_1$ | 0.0435 | $0.0000_4$ |
| 98.42 | .0414 | $.0000_3$ | .0418 | $.0000_3$ |
| 99.71 | .0410 | $.0000_4$ | .0412 | .... |
| 200.66 | .0390 | $.0000_6$ | .0394 | .... |
| 301.13 | .0368 | $.0000_6$ | .0376 | .... |
| 406.88 | .0344 | $.0000_6$ | .0351 | .... |
| 489.86 | .0303 | $.0000_3$ | .0312 | .... |
| 605.67 | .0251 | $.0002_8$ | .0265 | .... |
| 700.38 | .0195 | $.0002_7$ | .0224 | $.0001_9$ |

The measurements with a flowing junction are given in the second column of Table I, and the maximum values after the flow is stopped in the fourth column. It was noted in the earlier paper that the electromotive force of a similar cell, but with no sucrose, increases 0.3 mv. when the flow is stopped, and that the amount of this change is independent of the acid concentration.[5] When sucrose is added to the acid this difference increases to 3.0 mv. for the solution containing 700 g. per liter, and the time required to reach the maximum value is not changed. Although this effect makes the readings with the solutions flowing more erratic and sensitive to the rate of flow, it is not difficult to fix the average value to 0.1 mv., as the small deviations from the mean values show. However, since the difference between the potentials at two types of junction changes, one at least of the potentials must also change. It is probable that both potentials change in the same direction, perhaps by several millivolts, but there is no indication of the direction of this change. Since one millivolt in the potential of this cell corresponds to a 4.5% change in activity, it is apparent that the uncertainty in activity values determined with the use of a liquid junction must be large.

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[2] Scatchard, This Journal, **47**, 696 (1925).

[3] I wish to thank Professor H. A. Fales of Columbia University for the gift of the sugar used.

[4] Scatchard, This Journal, **47**, 641 (1925).

[5] See correction, *ibid.*, **47**, 3107 (1925).

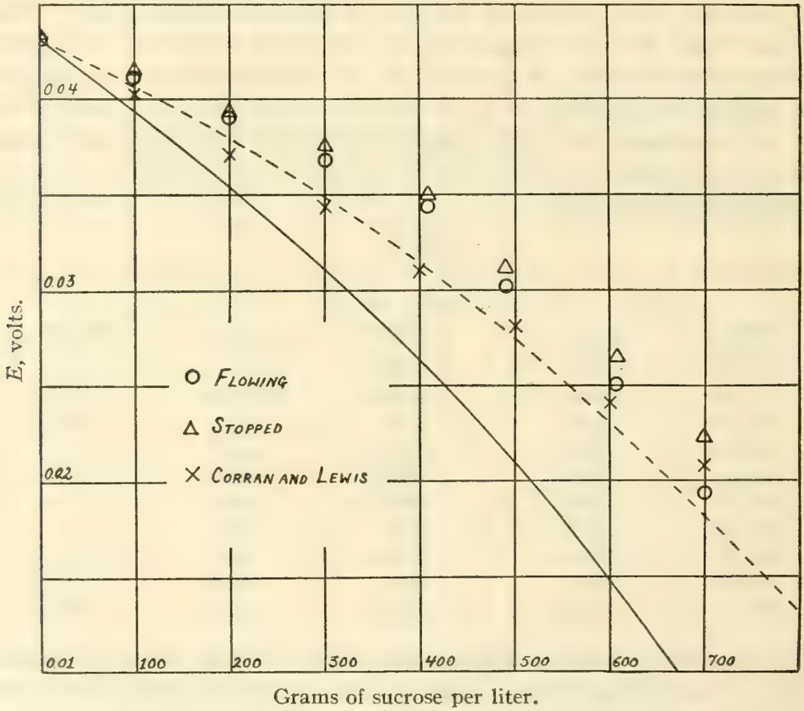

Fig. 1.—Hg | HgCl, KCl (satd.) | HCl (0.1012 *N*), sucrose, AgCl | Ag. Broken line, $\sqrt{A_H \times A_{Cl}}$. Full line, $\sqrt{A_K \times A_{Cl}}$.

In Fig. 1 the values of the electromotive force with flowing junction are represented by circles, and the maximum values without flow by triangles. The measurements of Corran and Lewis[6] on the cell Ag | AgCl, HCl (0.5 *N*) | KCl (satd.) | HCl (0.1 *N*), sucrose, AgCl | Ag, plus a constant to give agreement in the solution without sucrose, are represented by the crosses. The curves in this figure will be discussed in a later section.

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[6] Corran and Lewis, This Journal, **44,** 1673 (1922).

Part of the difference between my measurements and those of Corran and Lewis may be attributed to the fact that their saturated potassium chloride bridge contained sucrose in concentration about half that in the acid solution.

It is probable that the electromotive force of this cell, as of those to be discussed later, changes somewhat as the sucrose is inverted. The effect should be small during the short time required for measurement, and not greater than the deviation from the mean of the individual values. It is probably responsible for the fact that the deviations are larger for the last two solutions, but no attempt was made to study it quantitatively, or to correct the measured values for it.

## Cells Without Liquid Junction

The electromotive force at 25° of the cell Pt, $H_2$ | HCl ($c_1$), sucrose ($c_2$), AgCl | Ag was measured with the Clark type rocking hydrogen electrode previously described.[4] The solutions and silver chloride electrodes were prepared with those used in the cells with liquid junction. On each solution two measurements were made with different hydrogen electrodes but with the same silver chloride electrode. For reasons to be discussed below it was necessary to continue the rocking of the hydrogen electrode while the measurements were made. Otherwise the technique was the same as that described in the earlier paper. Measurements were also taken after the rocking had ceased for a definite time, and in some cases ith the electrode stationary but with hydrogen bubbling through the solution.

Since the completion of these experiments Taylor and Bomford[7] and Pennycuick[8] have noted that the electromotive force of the cell with a hydrogen electrode and a saturated potassium chloride bridge changes during the inversion of sucrose in the direction indicating an increasing activity of the hydrogen ion. The electromotive force of this cell changes similarly. The change was studied only with the solution containing 700 g. per liter. In the other solutions the change is much smaller and negligible for the short times between the mixing of the solutions and the measurements.

For the most concentrated solution the change for complete inversion is about 10 mv. From the rate of inversion measured by Moran and Lewis[9] this should give a change of about 0.01 mv. per minute at the start of the reaction. The measurements during the course of the reaction and the calculated values at the time of mixing are given in Table II.[10] Part of

[7] Taylor and Bomford, *J. Chem. Soc.*, **125**, 2016 (1924).

[8] Pennycuick, This Journal, **48**, 6 (1926).

[9] Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922).

[10] The values at the time of mixing depend somewhat upon the assumption as to the functional relationship between the electromotive force and the fraction of the sugar inverted. If the change in electromotive force is due to a change in the total number of moles, the activity of the ions should be (approximately) a linear function of the

the irregularity shown in the table may be due to the fact that the temperature, except at the time of the electromotive-force measurements, was not accurately controlled.

Table II

Effect of Reactions on Potential in Solutions Containing 700 G. of Sucrose per Liter

| Expt. | Time, min. | % Inverted | Reading, volts | Average variation from mean | Reading corr. to zero time |
|---|---|---|---|---|---|
| A | 102–114 | 13.9 | 0.3044 | $0.0000_1$ | 0.3059 |
| | 116[a] | .. | .3032 | .... | .... |
| B | 164–179 | 21.2 | .3017 | $.0000_2$ | .3044 |
| | 447–460 | 46.6 | .2997 | $.0000_1$ | .3054 |
| C | 505–517 | 50.6 | .3003 | $.0000_0$ | .3064 |
| | 1500–1512 | 87.5 | .2964 | $.0000_4$ | .3054 |
| | 1515[a] | .. | .2957 | .... | .... |
| | | | | Av. | .3055 |

[a] Rocking stopped immediately after last reading.

The measurements indicate that another chemical action is taking place at the hydrogen electrode. When the shaking was stopped the electromotive force decreased at the rate of 0.1–0.7 mv. per minute. The rate of decrease appeared nearly independent of the sucrose concentration, but varied greatly with some factor not controlled in these experiments. It was always many times the change due to inversion. When the shaking was resumed the electromotive force rose rapidly to its former value. Bubbling hydrogen around the electrode without shaking gave a steady value somewhat lower than that obtained when the cell was shaken. This behavior indicates clearly a reaction that uses up hydrogen and keeps the solution at the electrode unsaturated. The degree of unsaturation depends upon a balance between the rate of this reaction and the rate of diffusion to the electrode, and therefore upon the thickness of the diffusion layer. With the rocking electrode the diffusion layer is so thin that the error is probably small. The thicker diffusion layer with a bubbling electrode leads to a lower electromotive force. In either case the diffusion layer remains so nearly constant that the disturbance could not be detected with a single type of electrode. With neither bubbling nor rocking, the diffusion layer thickens continually as the reaction progresses so that the electromotive force is not constant. Examples of the change when the rocking is stopped are given by the rows marked *a* in Table II.

The most probable reaction that would use up hydrogen is the hydrogenation of sucrose or of the products of its inversion catalyzed by the platinum black of the electrode. A disturbance due to this reaction has

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fraction inverted; if the change is due to a change in the dielectric constant, the electromotive force should be a linear function. These two assumptions lead to average values which differ by about 1 mv. Probably both factors are operating. The values given in the table are averages for the two assumptions.

not previously been recorded, probably because all the earlier measurements have been made with bubbling electrodes only. I can find no record of a chemical study of this reaction, although the reaction of the sugars with oxygen in the presence of platinum black has long been known.

TABLE III

ELECTROMOTIVE FORCE OF THE CELL Pt, $H_2$ | HCl (0.1012 $N$), sucrose, AgCl | Ag

| Sucrose, g. per liter | $E$ meas. | Dev. from mean | $E$ calcd. | $d^{25}_4$ | $a_w$ without acid | Dielectric constant |
|---|---|---|---|---|---|---|
| 0.00 | 0.3516 | $0.0001_1$ | 0.3518 | 0.9986 | 1.0000 | 78.8 |
| .00 | .3518 | $.0000_1$ | .3518 | .9986 | 1.0000 | 78.8 |
| 98.42 | .3466 | $.0001_3$ | .3473 | 1.0364 | 0.9944 | 76.3 |
| 99.71 | .3461 | $.0002_3$ | .3472 | 1.0369 | .9943 | 76.3 |
| 200.66 | .3412 | $.0000_5$ | .3413 | 1.0752 | .9874 | 74.3 |
| 301.13 | .3352 | $.0000_2$ | .3350 | 1.1131 | .9789 | 72.3 |
| 406.88 | .3283 | $.0000_0$ | .3276 | 1.1526 | .9676 | 70.1 |
| 489.86 | .3222 | $.0000_6$ | .3211 | 1.1846 | .9565 | 68.3 |
| 605.67 | .3129 | $.0001_0$ | .3110 | 1.2245 | .9363 | 65.7 |
| 700.38 | .3055 | $.0005_5$ | .3018 | 1.2623 | .9143 | 63.4 |

The results for the cells without liquid junction are given in the second column of Table III, and are shown graphically by the circles in Fig. 2.

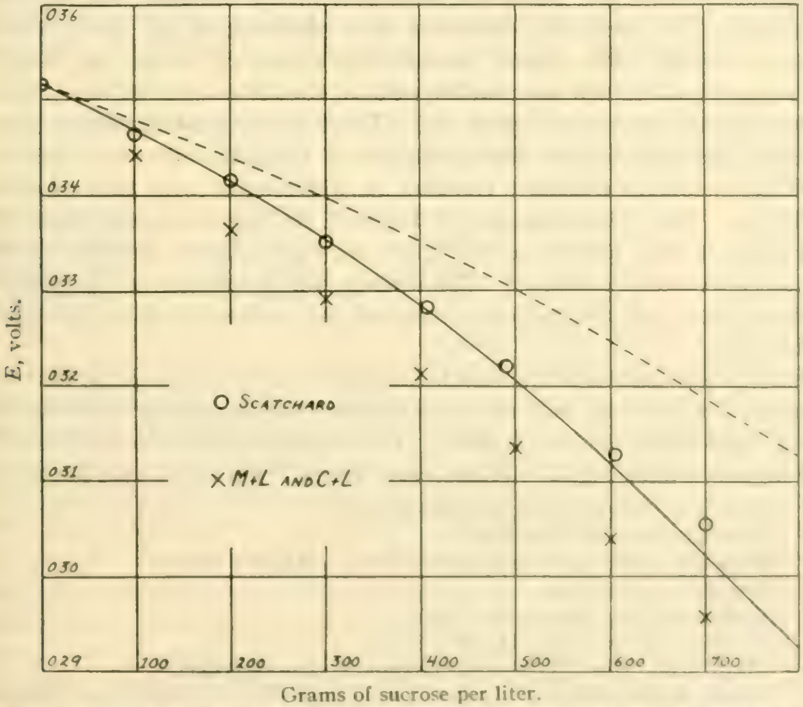

Fig. 2.—Pt, $H_2$ | HCl (0.1012 $N$), sucrose, AgCl | Ag. Broken line, no hydrate; full line, hydrate.

No attempt was made to correct any but the last for the effect of inversion, but the error from this cause should not be greater than twice the deviation from the mean given in the third column. The sum of the measurements of Corran and Lewis[6] on the cell Ag, AgCl, HCl (0.5 *N*) | KCl (satd.) | HCl (0.1 *N*), sucrose, AgCl | Ag and those of Moran and Lewis[9] on the cell Pt, $H_2$ | HCl (0.1 *N*), sucrose | KCl (satd.) | KCl (1.0 *N*), HgCl | Hg should give the same change on the addition of sucrose as the cell without liquid junction if their liquid junctions are reproducible. Their results, with a constant added to give agreement for the solution without sucrose, are represented by the crosses in Fig. 2. The discrepancy is several millivolts.

## Theoretical Interpretation

The electromotive force of the cell Pt, $H_2$ | HCl, AgCl | Ag in any solvent mixture whose average molecular weight, dielectric constant and vapor pressure of water are known may be calculated from the Debye theory of electrolytic solutions. The methods of calculation and the necessary assumptions are given elsewhere.[11] The water activity was determined by interpolating for concentration the values already interpolated for temperature[12] from the measurements of Berkeley, Hartley and Burton.[13] The dielectric constants were determined by interpolation from a smooth curve drawn through the values of Debye and Sack,[14] assuming that for each solution the ratio of the dielectric constant to that of water is the same at 25° as at 18°. These results agree excellently with those of Harrington[15] on dilute solutions if the latter are multiplied by 1.027 to make his dielectric constant of water agree with that of other observers. The measurements of Drude[16] at higher concentrations do not agree so well, and those of Fürth[17] are very different throughout the whole concentration range.[18] The density, water activity in the solution without acid and the dielectric constant for each solution are given in Table III.

If the mole fraction of the ions be calculated on the assumption that the sucrose and water do not react chemically, the agreement between the theory and measurements is poor. The curve for this case is shown by the broken line in Fig. 2. It has been shown,[19] however, that the vapor pressure of aqueous sucrose solutions may be simply and accurately explained by assuming that there is hydrate formation and that the vapor pressure of water is proportional to the mole fraction of the uncombined water. With these assumptions the number of moles of water per liter is equal to the number of moles of sucrose multiplied by the activity of the water and divided by one minus this activity. The values calculated with this assumption are represented by the full curve of Fig. 2 and are given in Col. 4 of Table III. The agreement between measurement and theory is very much better. The deviations in concentrated solutions increase regularly and are in the direction to be expected from the fact that the theory neglects the effect of the acid on the equilibrium between sucrose and water.

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[11] Scatchard, This Journal, **47**, 2098 (1925).

[12] Scatchard, *ibid.*, **45**, 1580 (1923).

[13] Berkeley, Hartley and Burton, *Phil. Trans.*, **218A**, 295 (1919).

[14] Private communication.

[15] Harrington, *Phys. Rev.*, **8**, 581 (1916).

[16] Drude, *Z. physik. Chem.*, **23**, 267 (1897).

[17] Fürth, *Ann. Physik*, **70**, 63 (1923); *Physik. Z.*, **25**, 676 (1924).

[18] Recent measurements of Kackel [*Ann. Physik*, **77**, 417 (1925)] are generally somewhat lower, with a maximum difference of 1% from the values quoted.

[19] Scatchard, This Journal, **43**, 2406 (1921).

The theory includes four reasons why the electromotive force should change with a change in the concentration of sucrose: the change in mole fraction due to the change in the total number of moles per liter; the change in the free-energy increase of the reaction $H_3O^+ = H^+ + H_2O$ due to the change in the activity of the water; the effect of the change in dielectric constant on the activity at infinite dilution; and the effect of the change in dielectric constant on the activity coefficient. Table IV shows the magnitude of each of these effects for the most concentrated solution, and shows also the effect of the two assumptions regarding the total number of moles.

Table IV

Factors in Effect of Sucrose on Electromotive Force (700 G. per Liter)

| | HCl | | KCl | |
|---|---|---|---|---|
| Factor | Hydrate | No hydrate | Hydrate | No hydrate |
| Mole fraction | −0.0429 | −0.0263 | −0.0429 | −0.0263 |
| Water activity | − .0023 | − .0023 | .0000 | .0000 |
| $E_N$ (inf. dil.) | − .0088 | − .0088 | − .0327 | − .0327 |
| Activity coeff. | + .0040 | + .0040 | + .0052 | + .0052 |
| Total change | − .0500 | − .0334 | − .0704 | − .0538 |

The electromotive force of the cell Ag | AgCl, KCl (0.1012 $N$) | K, Hg | KCl (0.1012 $N$), sucrose ($c$), AgCl | Ag was calculated in an exactly similar way, and the effects of the four factors for the most concentrated solution are shown in Table IV. If the addition of sucrose affected the activity of the potassium and chloride ions to an equal extent and did not change the liquid-junction potential, the change in electromotive force of the cell Hg | HgCl, KCl (satd.) | HCl (0.1012 $N$), sucrose ($c$), AgCl | Ag would be half the electromotive force of the above cell. This corresponds to the full curve of Fig. 1. The assumption of equal effect on the potassium and chloride ions demands a change in the liquid-junction potential of more than ten millivolts, which seems improbable. The measurements are fitted much better by assuming that the change in activity of the chloride ion is equal to the change in the mean activity of the ions of hydrochloric acid, represented by the broken line in Fig. 1. These results confirm the conclusions drawn from measurements on alcohol-water mixtures[11] that the effect of changing dielectric constant on activity cannot be the same for the potassium and the chloride ions, but the uncertainty as to the liquid-junction potential prevents more precise conclusions.

## Discussion

In spite of the difficulties of measurement it is believed that the measurements on the cell without liquid junction are accurate to a few tenths of a millivolt when the sucrose concentration is not greater than 500 g. per liter, and to a few millivolts for higher concentrations. This corresponds to an accuracy in the measurement of the mean activity of the ions of hydrochloric acid of about 0.5% below 500 g. per liter, and to a few per cent. above. The agreement with the theory is not quite so close, but it is as good as should be expected from the simplifying assumptions which were made.

The measurements with the cell with flowing junction are reproducible to the same precision, but their interpretation in terms of activities are uncertain to several millivolts on account of the lack of knowledge of the effect of sucrose on the liquid junction potential. Moreover, in this case theory gives no definite values with which the measurements might be checked. So the values of single ion activities in solutions containing sucrose are uncertain to many per cent., and it is evident that this uncertainty cannot be reduced without some radical improvement in experimental technique or in theoretical knowledge.

The values previously reported in the literature for the activity of the hydrogen ion in sucrose solutions are even more uncertain because they are probably not free from error due to irreproducible liquid-junction potentials and to the effect of the hydrogenation reaction on the potential at a bubbling hydrogen electrode. The new experimental evidence is thus directly contradictory to the conclusions which I drew elsewhere[12,20] that these values might be accepted as accurate.

This uncertainty as to the activity of the hydrogen ion in solutions containing sucrose makes inconclusive the attempts made by myself,[12,21] and others[9,22] to determine the mechanism of the inversion process by fitting the rates of reaction quantitatively with formulas containing this hydrogen activity. Even the difference between the change of liquid junction potential with flowing and with stationary junction amounts to 11% in the hydrogen activity between 0 and 700 g. of sucrose per liter, while the change in water activity in this range is less than 9%. Obviously the number of moles of water that enter into the reaction cannot be accurately determined.

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[20] Scatchard, THIS JOURNAL, **45,** 1716 (1923).

[21] Scatchard, *ibid.*, **43,** 2387 (1921).

[22] Jones and Lewis, *J. Chem. Soc.*, **117,** 1120 (1920).

## Summary

The electromotive forces of the cell Hg | HgCl, KCl (satd.) ¦ HCl, sucrose, AgCl | Ag with flowing junction and of the cell Pt, $H_2$ | HCl, sucrose, AgCl | Ag have been measured at 25° with 0.1012 *N* acid and sucrose concentrations ranging from 0 to 700 g. per liter.

The potentials at both hydrogen and silver-chloride electrodes change during the process of inversion. The potential at the hydrogen electrode is also affected by a hydrogenation of sucrose or of the products of its inversion. The liquid-junction potential appears to be considerably changed by the addition of sucrose.

This last phenomenon, and to a smaller extent the second one, introduces a large uncertainty into the measurement of single-ion activities in these solutions, and therefore into the determination of the mechanism of the inversion process.

The values of the second cell are interpreted by theory, and some theoretical implications of the measurements with the first cell are discussed.

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Contributions
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Serial No.
175. A Mass-Action Equation for Compressed Gases, with Application to the Haber Equilibrium Data.

by

Louis J. Gillespie

[Reprint from the Journal of the American Chemical Society, **48**, 28 (1926).]

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 175]

# A MASS ACTION EQUATION FOR COMPRESSED GASES, WITH APPLICATION TO THE HABER EQUILIBRIUM DATA

BY LOUIS J. GILLESPIE

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Recently the following equation was derived[1] for the fugacity ($f_e$) of a gas in a mixture, from the assumptions that at sufficiently low pressures the equilibrium pressure of a gas in a mixture (or its "partial pressure") approaches the mole fraction—total pressure product and the fugacity approaches the pressure.

$$RT\ ln\ f_e = \int_{p^\times}^{p} (\partial v/\partial n_1 - v_1/n_1)\mathrm{d}p + RT\ ln\ f_p + RT\ ln\ x_1 \tag{1}$$

Here $f_p$ is the fugacity of the pure gas at the total pressure of the mixture, $x_1$ is the mole fraction, $\partial v/\partial n_1$ is the partial molal volume of the gas in the mixture, and $v_1/n_1$ is the molal volume of pure gas, the molal and partial molal volumes being measured at the same pressure ($p$). The integration is at constant temperature and composition and is carried from a very low pressure $p^\times$ up to the total pressure of the mixture. Utilizing the definition of fugacity and adding and subtracting the term $\int_{p^\times}^{p}(RT/p)\mathrm{d}p$, we obtain

$$RT\ ln\ f_p = \int_{p^\times}^{p} (v_1/n_1)\mathrm{d}p + RT\ ln\ p^\times = \int_{p^\times}^{p} (v_1/n_1 - RT/p)\mathrm{d}p + RT\ ln\ p \tag{2}$$

Substituting in Equation 1 and simplifying, we have

$$ln\ f_e = (1/RT)\int_{0}^{p} (\partial v/\partial n_1 - RT/p)\mathrm{d}p + ln\ px_1 \tag{3}$$

To find the mass action expression, let $\nu_1$ denote the stoichiometrical coefficient of Substance 1 in a chemical equation, these coefficients being taken negative for disappearing species, and let $K_p$ and $K_f$ be the usual mass action expressions in terms of "partial pressures" ($px_1$) and fugacities, respectively. Summation for all the species gives us

$$\Sigma\nu_1\ ln\ f_e = ln\ K_f = ln\ K_p + (1/RT)\Sigma\nu_1 \int_{0}^{p} (\partial v/\partial n_1 - RT/p)\mathrm{d}p \tag{4}$$

Equation 4 is a general mass action expression for pressure and concentration effects at constant temperature, since $K_f$ must be a function of the temperature alone. The integration is subject to the same conditions as before, the constant compositions being equilibrium compositions.

[1] Gillespie, THIS JOURNAL, **47**, 305 (1925).

We lack data for evaluating the partial molal volumes and can use Equation 4 only after simplifying assumptions. The simplest such assumption is that the partial molal volume does not vary with the composition. Equation 4 shows that in this case, and not in general otherwise, the ordinary $K_p$ is constant with varying concentrations at constant $T$ and $p$. In this case the partial molal volume must be equal to the molal volume of pure gas at the same temperature and pressure, since pure gas is a special case of particular composition. Therefore Equation 1 reduces to the fugacity rule given by Lewis and Randall[2] and Equation 4 reduces to

$$\log K_p = \log K_f + (1/2.3\ RT)\Sigma\nu_1 \int_0^p (RT/p - v_1/n_1)\mathrm{d}p \qquad (5)$$

Equation 5 may be derived directly from the rule of Lewis and Randall. This rule requires therefore that $K_p$ be a function of the temperature and pressure only, and this, no matter what may be the equations of state for the individual pure gases.

We may introduce another simplifying assumption, that $RT/p - v_1/n_1$ is constant during the integration, equal to its limiting value at low pressures $(A_1/RT) - \beta_1$, which is to be calculated from the Keyes equation. This gives us

$$\log K_p = \log K_f + (\Sigma\nu_1 A_1)/(2.3\ R^2)\cdot p/T^2 - (\Sigma\nu_1\beta_1)/(2.3\ \mathrm{R})\cdot p/T \qquad (6)$$

## Applications to the Haber Equilibrium

Equation 6 has been applied to all the $K_p$ data given by Larson and Dodge[3] and Equation 5 has been applied to as many isotherms as seemed necessary to check the second simplifying assumption. The constants considered (until very recently) as best in the Keyes equation

$$p = RT/(v - \beta\ 10^{-\alpha/v}) - A/(v + l)^2 \qquad (7)$$

are given in Table I, in units of cc. per mole, atmospheres and centigrade degrees absolute ($T = t + 273.13$).

TABLE I

CONSTANTS OF THE KEYES EQUATION OF STATE

| Constant | $A$ | $l$ | $\beta$ | $\alpha$ |
|---|---|---|---|---|
| $NH_3$ | $8.5408.10^6$ | 33.93 | 135.7 | 68.21 |
| $N_2$ | $1.2747.10^6$ | 8.277 | 43.082 | 8.723 |
| $H_2$ | $0.15883.10^6$ | −2.384 | 19.385 | 2.539 |

$R$ was taken as 82.058 cc. — atm./mole. An accurate value was taken for the natural log 10. The ammonia constants are lately determined by Beattie and Lawrence,[4] the nitrogen constants are given by Smith and Taylor,[5] and the hydrogen constants are those preferred by Keyes, Townsend and Young.[6]

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[2] This rule is $f_1 = f_p x_1$. The equivalence of this rule and of the rule of additive volumes at any one temperature was shown in Ref. 1. It may be well to point out here that the part of the conclusions given in Ref. 1 dealing with heat content is based on a faulty proof which was added in a final revision of the manuscript and does not affect any other section of the discussion. A note of correction appeared in THIS JOURNAL in December, 1925.

[3] Larson and Dodge, THIS JOURNAL, **45**, 2918 (1923). The values for 300 atmospheres are given by Larson, *ibid.*, **46**, 367 (1924).

In these various references the volume unit is the cc. per gram.

$K_p$ is written for the reaction producing 1 mole of ammonia. Log $K_f$ was obtained from the empirical equation recently given[7] by putting $p = 0$. Equation 6 becomes then numerically

$$\log K_p = 2679.35/(t + 273.10) - 5.8833 + 494.38\, p/T^2 - 0.4503\, p/T \qquad (8)$$

The results are given in Table II, together with those of the check calculations from Equation 5. In applying Equation 5 the complete Keyes equation was used for the integrals. It was observed that the slopes of the curves: $RT/p - v_1/n_1 = f(p)$ do not approach zero at low pressures[8] except at a unique temperature, which is for the van der Waals equation one-half the Boyle-point temperature. Nevertheless the variation is not too great. It is greatest from a percentage standpoint for ammonia but the area for ammonia is curiously not so important as that for nitrogen and especially for hydrogen.

The individual areas were compared with the corresponding areas computed with constant ordinate and it was found that the agreement between Equations 5 and 8 did not depend on compensation of errors to any significant degree.

At the Boyle-point the ordinate $RT/p - v_1/n_1$ is zero at zero pressure. For a gas near the Boyle-point, the value of the ordinate varies much with the pressure (in this case passing through a minimum at about 100 atm.), but the ordinate remains small and the area is not so important if more nearly perfect gases are also involved in the reaction. For such gases, which are at temperatures above the Boyle-point, the ordinate becomes greater at higher temperatures, but also more constant.

It appears probable that Equation 6 will in general be a fairly good approximation of Equation 5, except in the case that one of the gases is at temperatures rather far *below* its Boyle-point.

[4] Lawrence, *Thesis, Massachusetts Inst. Techn.*, **1924**.

[5] Smith and Taylor, THIS JOURNAL, **45,** 2107 (1923).

[6] Keyes, Townsend and Young, *J. Math. Phys. Massachusetts Inst. Techn.*, **1,** 243 (1922).

[7] (a) Gillespie, *ibid.*, **4,** 84 (1925). (b) The equation is: $\log K_p = (2679.35 + 1.1184\, p)/(t + 273.10) - (5.8833 + 0.001232\, p)$.

[8] Diagrams from the Keyes or van der Waals equation do not resemble in this respect Fig. 2, p. 195 of Lewis and Randall's "Thermodynamics," (McGraw-Hill Book Co., New York, **1923**) and no sudden changes of slope have been seen. The tangent at $p = 0$ is given for the Keyes equation by $\partial/\partial p(RT/p-v) = A^2/(RT)^3 - 2A(\beta + l)/(RT)^2 + 2.3\, \alpha\beta/RT$. This expression was confirmed by the plots. By putting $\alpha = l = 0$ and $\beta = b$, we get the expression for the van der Waals equation. The approximate integration may be in general improved by use of this expression with due caution as to maxima or minima.

15

TABLE II

$K_p$ CALCULATED AND OBSERVED AT VARIOUS PRESSURES AND TEMPERATURES (CENTIGRADE)

| | Temperature | 325° | 350° | 375° | 400° | 425° | 450° | 475° | 500° |
|---|---|---|---|---|---|---|---|---|---|
| 10 atm. | Eq. 8 | 0.0401 | 0.0264 | 0.0180 | 0.0126 | 0.00909 | 0.00669 | 0.00502 | 0.00384 |
| | Obs. | .0401 | .0266 | .0181 | .0129 | .00919 | .00659 | .00516 | .00381 |
| | Eq. 5 | ... | .0264 | .0180 | ... | .... | .00669 | .... | .00384 |
| 30 atm. | Eq. 8 | ... | .0271 | .0184 | .0129 | .00924 | .00679 | .00509 | .00389 |
| | Obs. | ... | .0273 | .0184 | .0129 | .00919 | .00676 | .00515 | .00386 |
| | Eq. 5 | ... | .0271 | .0184 | ... | .... | .00678 | .... | .00389 |
| 50 atm. | Eq. 8 | ... | .0278 | .0188 | .0131 | .00940 | .00689 | .00516 | .00393 |
| | Obs. | ... | .0278 | .0186 | .0130 | .00932 | .00690 | .00513 | .00388 |
| | Eq. 5 | ... | .0277 | .0188 | ... | .... | .00688 | .... | .00393 |
| 100 atm. | Eq. 8 | ... | ... | .0199 | .0138 | .00981 | .00715 | .00533 | .00404 |
| | Obs. | ... | ... | .0202 | .0137 | .00987 | .00725 | .00532 | .00402 |
| | Eq. 5 | ... | ... | .0197 | ... | .... | .00711 | .... | .00403 |
| 300 atm. | Eq. 8 | ... | ... | ... | ... | .... | .00830 | .00606 | .00453 |
| | Obs. | ... | ... | ... | ... | .... | .00884 | .00674 | .00498 |
| | Eq. 5 | ... | ... | ... | ... | .... | .00829 | .... | .00452 |

Table II shows an excellent agreement between the observed data and the figures calculated from the approximate Equation 8 up to and including 100 atmospheres. A single error as large as 2.8% occurs, and this at 475°, 10 atmospheres where experimental error is responsible. Elsewhere there are one or two errors of 1.5%, at 375° and 100 atmospheres, and at 450°, 100 atmospheres. The results of the more exact Equation 5 support in general the agreement, the worst errors being at 100 atmospheres; 2.3% at 375° and 2.0% at 450°. The agreement is good, though a comparison of the values, especially with the aid of the empirical equation, makes it evident that at the higher pressures the errors become consistently greater as the temperature decreases.[9] One concludes that the equations and hence the Lewis and Randall fugacity rule are verified excellently up to 50 atmospheres and well at 100.

Equation 6 was further tested by making reasonable variations in the Keyes constants. For instance, changing only those for ammonia and making use of $A$ and $\beta$ values from Keyes and Brownlee[10] for ammonia, the coefficients of $p/T^2$ and $p/T$ become 591.00 and $-0.5955$, respectively. Making use of the best values for ammonia and nitrogen but using values for hydrogen derived by Keyes, Townsend and Young[6] from Onnes' data alone, the coefficients of $p/T^2$ and $p/T$ become 492.62 and $-0.4362$, respectively. Although the new sets of coefficients differ considerably, they represent the data through 100 atmospheres just as well as do those from the best constants when put in Equation 6. When $A$ and $b$ were calculated by van der Waals' theory from critical data no agreement was found, the calculated pressure effects being considerably greater than the observed effects. All this is as it should be if the agreement reported is not accidental.

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[9] On recalculating precisely $K_p$ from the percentage of ammonia, I find in this corner of the field small differences up to 0.8% of $K_p$ in the direction to increase this trend.

[10] Keyes and Brownlee, "Thermodynamic Properties of Ammonia," John Wiley and Sons, New York, 1916.

Table II shows that at 300 atmospheres we find deviations of 6 to 10%. A certain discrepancy was expected since empirical study has shown an experimental discrepancy between the high- and the low-pressure data.[7a] We cannot apply the equations to still higher pressures because here the calculated pressures for ammonia begin to decrease with diminution of volume. This happens at 450° and 361 atmospheres.

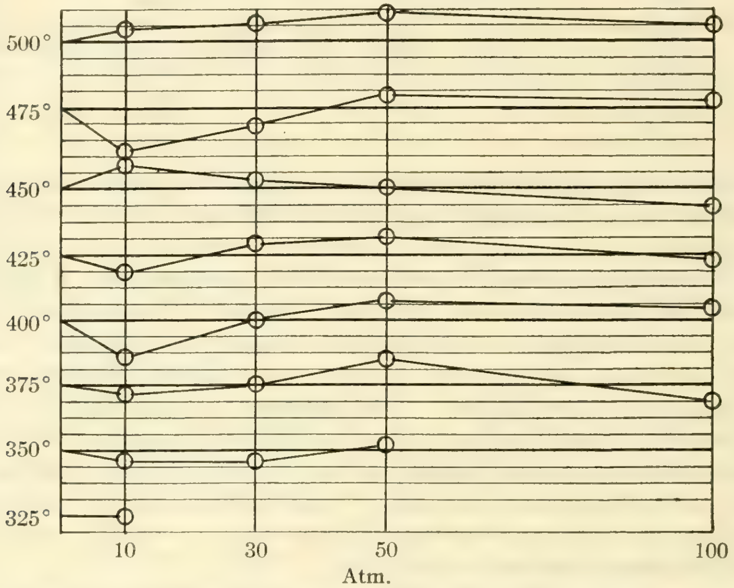

Fig. 1.—Deviations, in percentages of calculated from observed $K_p$ values, as functions of the pressure at different temperatures. Base lines of zero deviation are in heavy lines opposite the temperatures. One scale division = 1%.

Recently the work of Smith and Taylor on nitrogen has been recalculated and the following values have been given me by Professor Keyes: $A = 1.2651 \cdot 10^6$ and $\beta = 46.429$. These values together with the corresponding values for ammonia and hydrogen from Table I, give the numbers 494.69 and —0.4414 for the coefficients of $p/T^2$ and $p/T$, respectively, in Equation 6. Equation 6 with these numbers in it satisfies the data probably a little better than before, as a certain trend in the deviations has nearly or quite disappeared. Fig. 1 shows the deviations, in percentages, of the calculated from the observed values of $K_p$. Fig. 1 illustrates well the principal result of this paper, if it is remembered that the irregularities in the deviations are entirely due to the data, since the equation furnishes smooth results. The greatest deviation is 2.7% at 10 atm., 475°; the next is 1.8% at 50 atm., 500°. Larson and Dodge stated that their maximal error might reach 3%, though the probable error should be much smaller. Up to 100 atmospheres, therefore, the representation appears to be within the experimental error. At 300 atmospheres, and at 450°, 475° and 500°, the deviations are 5, 9, and 8%, all negative.

Any of the equations will furnish $K_p$ values at pressures lower than 10 atmospheres much within the experimental error, which is greater because of the sensitivity of $K_p$ to errors of analysis at low pressures.

## Summary

1. A general mass action expression (A) is derived for compressed gases at constant temperature.

2. By assuming that the partial molal volumes can be replaced by the molal volumes a simpler equation (B) is obtained, which can also be derived from the Lewis and Randall fugacity rule.

3. The equation was further simplified to the approximate relation (C):

$$\log K_p = \log K_f + (\Sigma\nu_1 A_1)/(2.3\ R^2)\cdot p/T^2 - (\Sigma\nu_1\beta_1)/(2.3\ R)\cdot p/T \qquad \text{(C)}$$

where $K_f$ is the value of $K_p$ for $p = 0$, and $A$ and $\beta$ are constants in the Keyes equation of state.

4. Using the Keyes equation of state as the means for extrapolating existing $p - v - t$ data to the region in question, Equations (B) and (C) were applied to the Haber equilibrium data obtained by the Fixed Nitrogen Research Laboratory and were found to represent the data within the experimental error to and including 100 atmospheres.

5. These results furnish an excellent verification of the fugacity rule proposed by Lewis and Randall, which rule has not hitherto been subjected to any very exacting experimental test.

6. These results lead thermodynamically to the expectation that for the Haber equilibrium $K_p$ will not vary greatly with composition at constant temperature and pressure up to about 100 atmospheres.

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# THE PALLADIUM-HYDROGEN EQUILIBRIUM AND PALLADIUM HYDRIDE

by

Louis J. Gillespie and Flemmon P. Hall

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# THE PALLADIUM-HYDROGEN EQUILIBRIUM AND PALLADIUM HYDRIDE[1]

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After Graham reported the great absorptive capacity of palladium for hydrogen, the relationship between the two elements became the subject of much experimental study. Besides the interest of the possible compound $Pd_2H$, the relationship may have bearing on the great catalytic activity of palladium in reduction.

In 1874 Troost and Hautefeuille[2] reported the hydride $Pd_2H$. They brought more evidence forward than they considered necessary. When the phase rule was announced a few years later, it could be seen that their evidence, though almost complete, was not quite so. A number of workers have since tried to furnish a complete proof, but without success.

Pressure-composition diagrams, obtained by Roozeboom and by Hoitsema for the system Pd-H, were presented by the latter.[3] Hoitsema concluded that the system was isothermally univariant throughout and that, therefore, the compound $Pd_2H$ was not formed. In coming to this conclusion he was not in a position to explain the possibility of observations such as those of Troost and Hautefeuille. Nevertheless, his conclusion as to the nonexistence of the hydride has been generally accepted; and although many writers show a feeling that all is not right, we have learned of only one writer[4] (up to 1925) who regards the existence of $Pd_2H$ as an open question.

Sieverts[5] obtained curves very similar to those of Hoitsema. The curves show no nonvariant portions and the "breaks" are not sharp.

Holt, Edgar and Firth[6] postulate the presence of an amorphous and a crystalline variety of palladium but have hardly demonstrated the presence of these two distinct modifications. The work of A. E. Oxley[7] on the determination of the magnetic properties of palladium that has been treated with hydrogen seems to indicate some sort of chemical union between the two components. Likewise the work of Wolf[8] on the electrical conductivity of the system seems to indicate some form of chemical union.

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[1] This paper is an abstract of a thesis presented by F. P. Hall in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology. We wish to acknowledge the assistance of Mr. Emanuel Tarplin during part of the experimentation.

[2] Troost and Hautefeuille, *Compt. rend.*, **78**, 686 (1874); *Ann. chim. phys.*, [5] **2**, 273 (1874).

[3] Hoitsema, *Z. physik. chem.*, **17**, 25 (1895).

[4] A. E. Hill, in Taylor's "Treatise on Physical Chemistry," D. van Nostrand Co., NewYork, **1924**, vol. 1, p. 437.

[5] Sieverts, *Z. physik. Chem.*, **88**, 451 (1914). Especial reference to p. 470.

[6] Holt, Edgar and Firth, *ibid.*, **82**, 513 (1913).

[7] Oxley, *Proc. Roy. Soc.*, **101A**, 264 (1922).

X-ray work by Yamada[9] and by McKeehan[10] seems to give evidence of the formation of solid solutions rather than a compound in this system. However, the evidence does not seem conclusive, as the X-ray results are negative in character rather than positive.

We undertook the present work feeling that Hoitsema's diagrams could not represent true equilibrium conditions, even though we were not able to perceive where the difficulty lay.[11] After our work had been brought to a close, the paper of Lambert and Gates[12] appeared, giving pressure-composition diagrams. These diagrams show, for spongy palladium, very marked hysteresis effects. They prove abundantly that an equilibrium truly independent of time cannot be attained by operating isothermally at the usual temperatures on such material. We believe the same is true for every preparation of palladium that has ever been studied, including our own preparations. Lambert and Gates do not claim definite evidence of the hydride, $Pd_2H$, but they point out that their curves are not what would be expected if two solid solutions exist, since their descending isothermals "show 'breaks'" at approximately the same composition (about 0.53 atom of hydrogen per atom of palladium) at temperatures of 75°, 103° and 120°. It seems certain that these isothermals are not true equilibrium lines.

## Preparation of Materials

Palladium chloride was reduced to metallic palladium by the method of Wieland,[13] using sodium formate. The metal was converted into chloride again and purified through several crystallizations of the characteristic yellow salt, palladosammine chloride, by the method of Gutbier[14] used in atomic weight work. Following Gutbier, the metal was prepared by reducing the yellow salt in a stream of dry hydrogen at about 150°. Stronger heating was necessary to remove ammonium chloride, but the temperature was kept as low as possible. The stream of hydrogen was stopped, carbon dioxide was passed through to replace hydrogen and the metal was cooled in carbon dioxide. The metal was black, finely divided. It could be weighed without a special technique.

A sample of 1.9338 g. (*in vacuo*) of yellow salt treated in this way yielded 0.9746 g.

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[8] Wolf, *Z. physik. Chem.*, **87,** 588 (1914).

[9] Yamada, *Sci. Repts. Tôhoku Imp. Univ.*, [1] **11,** 451–454 (1922); *Phil. Mag.*, **45,** 241 (1923).

[10] McKeehan, *Phys. Rev.*, **21,** 334 (1923). This article contains an excellent bibliography on the system, palladium-hydrogen.

[11] Some preliminary work was done in this Laboratory by Taneichi Yoneda and by J. H. Perry. [Perry, *Thesis*, Massachusetts Institute of Technology, **1922.**]

[12] Lambert and Gates, *Proc. Roy. Soc.*, **108A,** 456–482 (1925).

[13] Wieland, *Ber.*, **45,** 484 (1912).

[14] Gutbier, *J. prakt. chem.*, (N. F.) **79,** 235 (1909).

of palladium. This is 50.398% of palladium. That calculated for $Pd(NH_3)_2Cl_2$ by 1921 atomic weights (Pd = 106.7) is 50.405%.

A portion of this palladium is called palladium A. Another portion was carried through the formate reduction and is called palladium B. Both preparations had thus been put through both separations, but the final mode of reduction was different, and it was thought possible that this would affect our results. Palladium B was not treated with carbon dioxide and was weighed in a vacuum.

The hydrogen was prepared by electrolysis of a 10% solution of sodium hydroxide, using a platinum anode and a nickel cathode. The hydrogen was then passed over heated platinized asbestos to remove oxygen and then over tubes of phosphorus pentoxide. These tubes were carefully exhausted, being well rinsed with hydrogen and well heated during the exhaustion process. We decided not to use a portion of palladium itself for a further purification of the hydrogen. The hydrogen generator was operated continuously to avoid introduction of nitrogen by diffusion.

Even 0.1% of nitrogen would have had an appreciable effect on the isotherms, except for the fact that all hydrogen withdrawn from the palladium during the experiments was discarded, thus largely eliminating any impurities at the same time.

## Description of the Apparatus

A simple water-jacketed volume buret with two calibrated marks, one for 4.6 cc. and one for 29 cc., was provided with a barometer column on which the pressure could be read with a meter stick. The buret had a two-way stopcock with large capillary leads. One lead connected with the hydrogen supply, the other with the reaction chamber. Pressures in the reaction chamber were read by means of the same barometer column, with a zero mark in the capillary lead. All zero corrections were determined when the pressure was the same on both columns in question.

The large volume space in the buret was used when it was necessary to remove hydrogen at low pressure. Hydrogen thus removed was pumped away through the barometer column and delivered into the open air.

Two separate apparatuses of this kind were set up and used, at the same time, in order to make use of the long time intervals required for reaching equilibrium. One was limited to work at 0°, using ice in a large Dewar tube. The other was provided with an oil thermostat, well-stirred and regulated.

The temperatures were read with mercury thermometers which were calibrated shortly after the experiments with a platinum resistance thermometer and found to be accurate to about 0.1°.

For work at the higher temperatures, a special manometer was constructed and the levels were read on a steel tape measure affixed close to the manometer column, which could be opened to the atmosphere in order to get another atmosphere of pressure.

All important volumes were determined by weighing mercury. The volume of one reaction chamber was about 4.8 cc.; of the other, which was used for high temperatures, about 7.7 cc.

For low temperatures, the reaction chamber was connected to the buret through a ground-glass joint which was submerged in the bath. For the higher temperatures, a fused joint in the capillary tube was necessary, but it introduced no appreciable volume error. All other joints in the apparatus were fused-glass joints.

## Mode of Conducting the Experiments

The general procedure before starting a run was to evacuate the reaction tube and heat it to about 400°, to cool and admit hydrogen and then to evacuate while the tube was at about 400°. This was to remove any traces of oxygen or other gases. The tube while hot was evacuated with a mercury diffusion pump until the McLeod gage showed 0.001 mm. or less. This procedure was repeated several times before a run was started. Hydrogen was then admitted to the volume buret and after its pressure, volume and temperature were measured it was admitted to the reaction tube and the pressure of the palladium-hydrogen system was measured. The volume of the dead space in the reaction tube was known, and the amount of gas absorbed by the palladium could be calculated, since the dead space was at the same temperature as the palladium, except for the very small and known volume of the part of the capillary outside of the bath, which was assumed to be at room temperature.

About 0.2 g. of palladium, weighed accurately, was used in each experiment.

## Summary of the Experiments at Zero Degrees

Referring to Fig. 1-A, a zero-degree isotherm, OABCD, was determined by adding hydrogen in small quantities, keeping the system constantly at 0°. The pressures from O to B quickly came to equilibrium, as a rule, but after a little progress along AB, the pressure equilibration became more and more sluggish until it soon became evident that it is impossible in this way to realize a state of equilibrium truly independent of the time over any large range of composition. Points from B to C were therefore plotted as soon as the pressure had become reasonably constant. The system was permitted to remain for a day or two at the point C. From C to D, hydrogen was then withdrawn, until at D the pressure was so low that it became impracticable with the given apparatus to withdraw significant masses of hydrogen.

Faced with this impasse, we finally heated the system to about 200°, for a few minutes. On cooling, the pressure soon arrived at the value E, to our gratification. A second heating did not further displace the pressure from the value E. In like manner, withdrawal of hydrogen brought the system to point F, and a brief heating as before caused the system to arrive at point G after the lapse of a reasonable time. By this means as many points could be obtained as we chose, all points on the line EA.

Such heat treatment is evidently of great value in permitting equilibrium to be established after removal of hydrogen from the system; for it will be observed that the points E, G lie at the same pressure level (within 0.1 or 0.2 mm.) as the point A, which was secured without the aid of any variations of temperature. It is, therefore, impossible that an equilibrium at high temperatures is being "frozen."

We have determined the section OA and AB many times. The angle A was generally quite sharp, although sometimes it was rounded, in which case the section AB was not quite horizontal. Twice it has happened that no change of curvature at all was found at A, the isotherm rising as a continuous adsorption curve. After one such occurrence the palladium A was treated in an electric furnace at 200° with hydrogen, then with carbon dioxide. After being cooled in carbon dioxide the metal was introduced again into the apparatus, exhausted and treated with hydrogen, re-exhausted in the usual way and made the subject of a new experiment. In this new experiment the angle A was obtained. We think that such continuous isotherms are more likely to occur when the metal is produced by reduction with sodium formate.

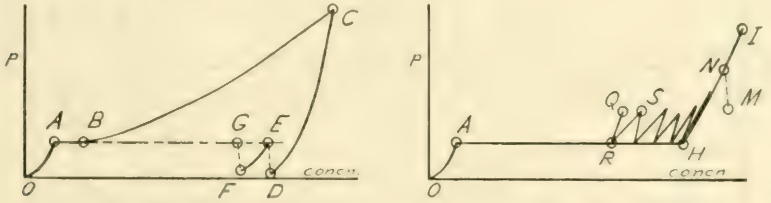

Fig. 1-A. Fig. 1-B.

Illustrating experiments at 0°.

Ordinarily, one heat treatment gave the full effect, but other treatments were usually given to make sure that the maximal effect was in fact reached. The precise temperature did not seem to matter, and after the first few treatments a bath of boiling mercury was always used.

Such heat treatment appears not to have been tried by any previous investigators. It has permitted us for the first time to trace rational phase diagrams for the Pd-H equilibrium.

We have, therefore, used the heat treatment with confidence in the determination of the end H of the horizontal isotherm and the rising isotherm HI. See Fig. 1-B. If the system was in the state Q and hydrogen was withdrawn, on heating the system each time before beginning the pressure measurements, various points on the line QR could be observed. (Further withdrawals would give points along RA.) If from R, hydrogen was added, points along RS could be traced. By alternating series of withdrawals with series of additions of hydrogen, the zigzag lines indicated in Fig. 1-B could be traced. These lines approached a limiting line, IH, which could be traced and retraced up and down, within the experimental error.

The point H was taken as the end of the horizontal part of the isotherm, and the line IH was taken to be the second ascending isotherm. In tracing these lines, the system was heated to 360° before each point was observed. The system was sluggish in this part of the field even after heating, the pressure becoming constant after one to three days, or sometimes longer. The heat treatment appeared of little or no benefit when adding hydrogen, but of great benefit when withdrawing hydrogen. If hydrogen is withdrawn in this region without heating, a point such as M may be observed; after heating the pressure rises in a reasonable time to a value N on the line IH.

Now it is, of course, possible that the line IH thus found is not quite the true equilibrium line on account of temperature disturbance. The method that gives it is, however, the same method that gives the line AH which is certainly correct (except possibly as to the point H) and we believe that the point H and the line IH are, therefore, substantially correct.

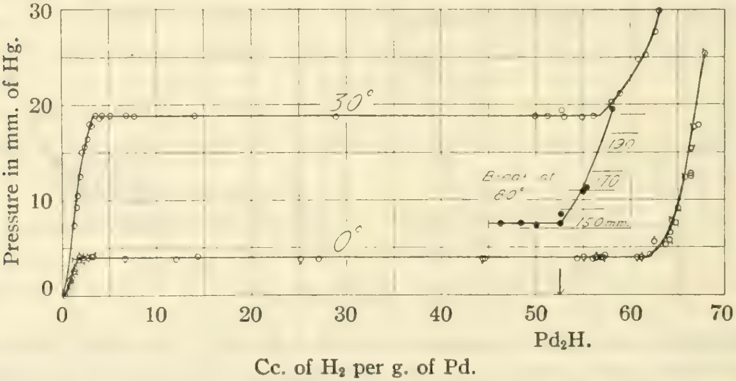

Fig. 2.—0° and 30° isotherms; with inset showing break at 80° with separate pressure but same composition scale. Plain circles on 0° isotherm represent palladium *A;* circles with one mark indicate palladium *B;* circles with two marks indicate the same result with both preparations.

The recent experiments of Lambert and Gates[12] may be taken to suggest the existence of a pure temperature effect, but we do not think such an inference is necessary. We think that the curious temperature effects observed by them after they had cooled their system and restored the temperature are explainable in terms of concentration disturbances. Such concentration disturbances, consisting of a withdrawal and an addition of hydrogen with respect to the solid mass, would be due to the effect of temperature on the gas in the dead space over the solid mass. Examination of their figures shows that, in any given part of the field, the effect of cooling and heating upon the pressure is in the same direction as the effect of adding and subtracting one unit of hydrogen isothermally.

A plot of the results at 0° is given in Fig. 2. Both preparations of palladium were studied, and the curves coincide throughout, as the figure shows. The mode of final reduction to metallic palladium appears to have some influence indeed on the degree of sluggishness with which equilibrium is approached, but no influence on the final equilibrium.

The point H lies at 62 cc. of hydrogen per gram of palladium, representing an excess of 18% of hydrogen over the formula $Pd_2H$.

### Experiments at Other Temperatures

Similar complete isotherms were obtained at 30°, 80°, 160° and 180°, using only palladium finally reduced with hydrogen from the yellow salt.

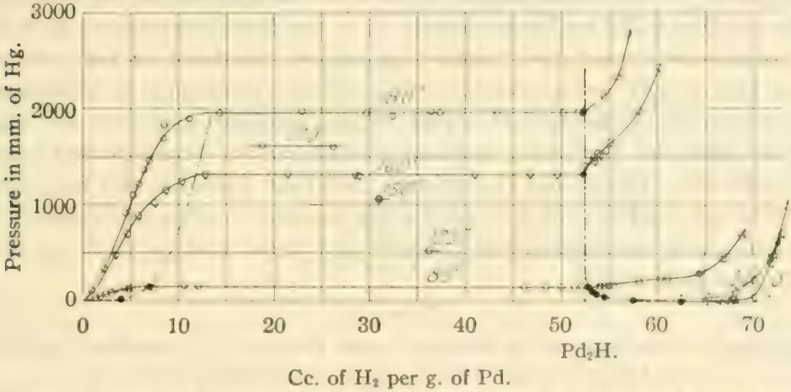

Fig. 3.—Plot of all results at relatively high pressures. The solid circles and the broken lines show the compositions of the coexistent solid phases as functions of the pressure.

Fig. 2 shows the 30° isotherm and also the break in the 80° isotherm on a suitable scale. Fig. 3 shows the isotherms at the three highest temperatures, as well as the high-pressure results on the 0° and 30° isotherms, which curiously appear to intersect.

Fig. 3 shows that the isotherms indicate the compound $Pd_2H$ at high temperatures. The break at 80° is located at a composition only 0.2 or 0.3% in excess of this compound, and at higher temperatures, at least up to and including 180°, the breaks occur at exactly the $Pd_2H$ composition, 52.5 cc. of hydrogen per gram of palladium, within the experimental error.

Certain of the discrepancies are due to the accumulation of volume errors in withdrawing and adding hydrogen many times before reloading. Points are also included which were obtained by variation of the temperature over part of the experimental range, such as the high point over the horizontal part of the 30° isotherm. Such points generally gave nearly correct values, although the system was not always heated to 360° after the variation of temperature.

## Comparison of the Pressure Data with Those of Previous Investigators

Our pressures along the horizontal isotherms differ from those of Troost and Hautefeuille and those of Hoitsema by 100 or 200 mm. of mercury at high temperatures.

Table I gives the pressure in millimeters of mercury, calculated from a smoothed graph for rounded temperatures, and for a few odd temperatures of interest in view of previous work. A plot was drawn, Fig. 4, representing the deviations: log $p$ (observed) $-$ $[(a/T) + b]$ as a function of $1/T$. In smoothing the observations it was assumed that a log $p$, $1/T$ plot is nearly straight at low temperatures but shows curvature at higher temperatures. If such smoothing is justified, our measurements are consistent either within 0.7% on the pressures or, at the lowest pressures, with discrepancies not exceeding 0.2 mm. The values calculated for temperatures from 100° to 120° are uncertain by 3%, due to arbitrariness in determining the curvature of the deviation plot. Our calculated pressures are much higher than the descending horizontal isotherms of Lambert and Gates. We infer that Troost and Hautefeuille and that Hoitsema did not obtain equilibrium, and in such an event a few hundred millimeters mean little, as is shown in the diagrams of Lambert and Gates working with one preparation of palladium.

TABLE I

PRESSURES IN MILLIMETERS OF MERCURY OVER HORIZONTAL ISOTHERMS, OBSERVED AND CALCULATED BY MEANS OF DEVIATION CURVE OF FIG. 4

| Temp., °C. | 0 | 30 | 75 | 80 | 100 | 103 | 120 | 160 | 180 |
|---|---|---|---|---|---|---|---|---|---|
| $p$ calcd. | 3.75 | 18.9 | 126.5 | 151.6 | 292 | 321 | 518 | 1327 | 1970 |
| $p$ obs. | 3.95 | 18.7 | ... | 152.6 | ... | ... | ... | 1326 | 1961 |

Table I is based on the experimental values given in Table II for the temperatures at which complete isotherms were determined. The corresponding deviations are shown by solid black circles in Fig. 4. Data

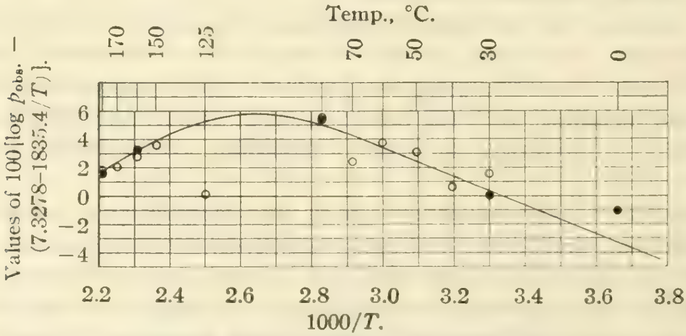

Fig. 4.—Deviation plot representing the effect of temperature on pressure over horizontal isotherms. Solid circles are from complete isotherms (Table II).

### Table II

### Equilibrium Pressures of Hydrogen over Palladium at Various Temperatures and Compositions

Composition $c$ in cc. of hydrogen (standard conditions) per gram of palladium. Pressure $p$ in mm. of ice cold mercury. Dotted lines indicate a complete removal of hydrogen.

Palladium A at 0°

| $c$ | $p$ | $c$ | $p$ | $c$ | $p$ | $c$ | $p$ | $c$ | $p$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.43 | 2.90 | 56.65 | 3.80 | 14.34 | 4.10 | 66.40 | 12.60 | 70.18 | 51.90 |
| 1.87 | 3.80 | 56.35 | 3.90 | ... | ... | 64.80 | 7.60 | 71.51 | 95.70 |
| 2.26 | 3.80 | 56.00 | 3.80 | 0.21 | 0.20 | 64.20 | 6.60 | 71.85 | 407.0 |
| 2.77 | 4.00 | 54.35 | 3.80 | 0.85 | 1.10 | 63.70 | 5.30 | 72.16 | 496.6 |
| 3.13 | 4.10 | 44.59 | 3.80 | 1.07 | 1.90 | 62.00 | 4.30 | 72.55 | 640.0 |
| 57.30 | 4.20 | 27.06 | 3.80 | ... | ... | 61.14 | 4.00 | | |
| 56.90 | 4.00 | 12.04 | 3.80 | 67.20 | 17.9 | 66.40 | 12.80 | | |

Palladium B at 0°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 68.00 | 43.8 | 66.7 | 17.7 | 57.00 | 4.00 | ... | ... | 1.83 | 4.08 |
| 60.70 | 4.0 | 67.9 | 25.4 | 56.36 | 4.00 | 0.36 | 0.30 | 2.11 | 4.02 |
| 61.20 | 4.0 | 66.4 | 15.4 | 44.37 | 3.80 | 0.83 | 1.70 | 3.30 | 4.10 |
| 62.5 | 5.6 | 64.15 | 5.8 | 25.14 | 3.80 | 1.27 | 2.60 | 65.02 | 9.13 |
| 64.4 | 7.8 | ... | ... | 6.63 | 3.90 | 2.21 | 3.80 | | |
| 65.8 | 12.4 | 55.02 | 4.0 | 1.38 | 3.60 | 2.76 | 4.00 | | |

Palladium A at 30°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 62.65 | 27.7 | 2.44 | 15.6 | 2.70 | 16.4 | 58.9 | 21.2 | 0.92 | 1.58 |
| 54.90 | 18.7 | 3.15 | 17.8 | 2.97 | 18.0 | 57.0 | 18.8 | 2.10 | 15.04 |
| 53.00 | 18.7 | 3.55 | 18.9 | 5.10 | 18.9 | 56.1 | 18.8 | 4.00 | 18.60 |
| 51.20 | 18.8 | 4.28 | 18.9 | 6.80 | 18.9 | 58.0 | 20.3 | 66.0 | 52.50 |
| 49.40 | 18.8 | ... | ... | 68.2 | 109.3 | ... | ... | 63.1 | 29.60 |
| 28.90 | 18.7 | 0.98 | 4.0 | 65.4 | 43.0 | 1.69 | 10.5 | 61.6 | 25.30 |
| ... | ... | 1.31 | 7.4 | 63.0 | 29.9 | 7.65 | 18.8 | 14.0 | 18.15 |
| 1.59 | 9.3 | 1.97 | 12.5 | 60.8 | 24.8 | ... | ... | | |

Palladium A at 80°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1.75 | 46.2 | 4.79 | 127.9 | 1.31 | 30.1 | 55.0 | 169.6 | 52.6 | 152.6 |
| 3.48 | 105.8 | 5.23 | 135.6 | 2.43 | 78.6 | 52.6 | 157.8 | 48.4 | 152.6 |
| 10.62 | 153.6 | 6.15 | 140.1 | 3.41 | 115.4 | 50.0 | 151.9 | | |
| 12.09 | 152.1 | 7.43 | 131.6 | 68.81 | 670.1 | 46.3 | 152.6 | | |
| 2.98 | 85.2 | ... | ... | 58.10 | 212.6 | 55.4 | 171.6 | | |

Palladium A at 160°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 3.43 | 488 | 10.39 | 1244 | 53.51 | 1508 | 49.55 | 1325 | 58.10 | 2000 |
| 4.65 | 700 | 12.82 | 1313 | 52.43 | 1403 | 46.77 | 1331 | 53.50 | 1460 |
| 5.87 | 888 | 53.84 | 1541 | 60.11 | 2434 | 41.03 | 1327 | | |
| 7.56 | 1016 | 52.82 | 1463 | 55.08 | 1657 | 21.48 | 1324 | | |
| 8.69 | 1153 | 54.67 | 1577 | 54.10 | 1527 | 52.30 | 1321 | | |

Palladium A at 180°

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 8.53 | 1733 | 43.29 | 1970 | 52.53 | 2006 | 4.52 | 919 | 8.49 | 1695 |
| 36.42 | 1979 | 37.35 | 1963 | 50.20 | 1966 | 5.28 | 1097 | 11.15 | 1896 |
| 32.39 | 1929 | 29.61 | 1960 | 54.50 | 2130 | 5.82 | 1219 | 14.31 | 1955 |
| 56.30 | 2380 | 56.95 | 2788 | 0.97 | 101 | 6.42 | 1363 | | |
| 51.78 | 1970 | 55.70 | 2333 | 2.15 | 336 | 6.98 | 1458 | | |

from Table III are not taken into account, the deviations for which are shown in Fig. 4 by rings.

Table III presents miscellaneous points determined by varying the temperature after having obtained equilibrium. Occasionally hydrogen was withdrawn, in which case (and not otherwise) the system was heated to 360° before taking pressure readings. In some cases, the change of composition due to temperature effect was enough to cause inaccuracy, but usually such a disturbing effect was not great. Some of these points refer to horizontal portions of the isotherms. When these points were plotted with respect to temperature, it was found that the value for 125° was quite bad, suggesting a mistake rather than an ordinary error. The other points are consistent only to about 3%. We have not been able to account for this poor consistency to our entire satisfaction. It is, therefore, possible that the consistency shown in Table I is illusory and that these figures also are uncertain to about 3%, especially from 80° to 150°. Excluding the value for 125°, these miscellaneous points confirm a curvature in the log $p$, $1/T$ plot.

### TABLE III

### MISCELLANEOUS EQUILIBRIUM MEASUREMENTS

$C$ and $p$ are as in Table II. $R$ or $L$ after a temperature value indicates that the temperature was raised or lowered to that value. H after a temperature figure indicates that hydrogen was withdrawn and the system heated to 360°. The experiments start with equilibrium at 160°.

| $T$ | $c$ | $p$ | $T$ | $c$ | $p$ | $T$ | $c$ | $p$ | $T$ | $c$ | $p$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 170 R | 18.87 | 1613 | 80 H | 66.83 | 446 | 60 L | 54.25 | 72.6 | 80 H | 51.40 | 152.8 |
| 180 R | 22.91 | 1975 | 80 H | 64.43 | 289 | 50 L | 54.51 | 47.6 | 70 L | 51.80 | 100.0 |
| 170 L | 26.24 | 1603 | 80 H | 61.11 | 241 | 80 R | 52.91 | 153.6 | 60 L | 52.15 | 71.4 |
| 160 L | 28.88 | 1314 | 80 H | 54.55 | 161 | 70 L | 53.41 | 102.0 | 50 L | 52.33 | 47.7 |
| 150 L | 31.02 | 1059 | 70 L | 55.05 | 110 | 60 L | 53.70 | 71.6 | 40 L | 52.58 | 29.8 |
| 160 R | 28.92 | 1308 | 60 L | 55.38 | 75.6 | 50 L | 54.10 | 47.6 | 30 L | 52.70 | 19.4 |
| 125 L | 36.20 | 525 | 50 L | 55.65 | 49.7 | 40 L | 54.30 | 29.6 | 30 H | 73.50 | 998 |
| 125 R | 36.22 | 522 | 40 L | 55.85 | 31.0 | 50 R | 53.10 | 48.1 | 30 H | 72.94 | 705 |
| 150 R | 31.00 | 1062 | 40 H | 54.71 | 29.5 | 60 R | 52.76 | 71.7 | 30 H | 71.68 | 441 |
| ... | ... | .. | 80 R | 53.44 | 155 | 70 R | 52.60 | 100.7 | 30 H | 70.10 | 222 |
| 80 H | 68.70 | 707 | 70 L | 53.94 | 104 | 80 R | 52.03 | 152.6 | 30 H | 68.21 | 108 |

On plotting for the first rising isotherms log $p$ against log composition, straight lines were not obtained. Thus Henry's law cannot be applied to show that hydrogen dissolves as atomic hydrogen or as any other fixed species. This was noted by Sieverts,[15] who equated the composition to the expression $k_1\sqrt{p} + k_2p$. We found that as the pressure approached zero the tangents on our plots approached 0.5, as if the first portions of hydrogen dissolve as atoms. This is in accord with the form of Sieverts' expression.

## Remarks on the Heat Treatment

Abundant evidence was obtained to show that hydrogen, expelled by heat, returns to the solids on cooling providing no excess of hydrogen is present. In the case of the data presented in Table II, upon which our diagrams and conclusions are based, the heat treatment was repeated to proved constancy of final pressure in about 80% of the points. Proof that constancy had been attained was occasionally omitted along the horizontal isotherm after four or five points along the isotherm had been determined by heating to constancy. It was also omitted after small *additions* of hydrogen along the second rising isotherms. In brief, evidence was secured for each part of each isotherm.

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[15] Ref. 5, p. 446.

The heating at 360° was for a period of two to four minutes. About one-half of the dead space was under the boiling mercury during the heating.

Our results refer, of course, to palladium which has recently been heated, but this is ordinarily the case in any event, because of the necessity of freeing the original palladium from oxygen and hydrogen.

## The Heat of Condensation of Hydrogen in Palladium

The heat effect, $-\Delta H$, for the reaction,

$$H_2\text{, gas, 1 atm.} + 4\text{Pd, 1 atm.} = 2(\text{Pd}_2\text{H})\text{, 1 atm. (decomposed)} \qquad (1)$$

can be calculated from our measurements, in simple fashion, by assuming that hydrogen is an ideal gas and that the energy effects due to changes of volume or pressure of the solids are negligible. The result refers to palladium hydride decomposed into two saturated solid solutions, but at 80° (and higher) one of these solutions is nearly pure $(\text{Pd}_2\text{H})_x$ and comprises nearly all the mass of the system.

Where the pressure is independent of the composition the ordinary Clapeyron equation can be used. Where the pressure varies along the isotherm, we can integrate the partial molal heat content of hydrogen at constant mass of palladium, thus obtaining the total heat.

Whether the pressure varies or not we shall have as final result:

$$-\Delta H = -2.3\,R\int_0^1 \left(\frac{\partial \log p}{\partial\, 1/T}\right)_c dn_1 \qquad (2)$$

where $n_1$ is the number of moles of hydrogen dissolved in the four gram atoms of palladium under an equilibrium pressure $p$ at a constant equilibrium temperature $T$. The quantity $-\Delta H$ is the heat evolved in the change of state written above[16] in Equation 1.

To obtain the above equation we start with one mole of hydrogen and imagine its pressure reduced to an infinitely low value at the constant temperature in question. The change in $H$ $(= U + PV)$ is zero for the perfect gas.

We now imagine the hydrogen put in contact with four atoms of palladium at the infinitely low equilibrium pressure. We then increase the pressure at constant temperature, reversibly, when $n_1$ will increase from zero to one. At the same time the pressure rises along the isothermal, becoming constant along the horizontal portion. When the gas phase has disappeared we raise the pressure to one atmosphere without any further appreciable change in $H$. We have to find $\int \mathrm{d}H$ for the addition of hydrogen ($n_1$) to the constant mass ($n_2$) of palladium at constant temperature.

---

[16] The heat evolved in the reversible addition of hydrogen equals $-\Delta H$ only when the isotherm is horizontal.

$$\mathrm{d}H = (\partial H/\partial n_1)_p \,\mathrm{d}n_1 + (\partial H/\partial p)_{n_1} \mathrm{d}p = T(\partial S/\partial n_1)_p \,\mathrm{d}n_1 = T(\partial S/\partial n_1)_{pTn_2} \mathrm{d}n_1 \quad (3)$$

We have noted that $(\partial H/\partial p)_{n_1} = 0 = \mathrm{d}n_2 = \mathrm{d}T$ and at constant pressure $\mathrm{d}H = T\mathrm{d}S$. $S$ is the entropy of the whole system. The mass of this system is constant, in the sense that no matter crosses its boundaries, therefore, $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$ and it would be incorrect to add a term $\mu \mathrm{d}n$. Planck[17] has evaluated $T(\partial S/\partial n_1)_{pTn_2}$. It is equal to $-L = -RT^2(\partial \ln p/\partial T)_c$, where subscript $c$ refers to constant composition and the minus sign is due to an opposite meaning of $\mathrm{d}n_1$. This gives Equation 2 when integrated.

The slope $(\partial \log p/\partial 1/T)_c$, multiplied by $-4.58$, gives the (differential) heat evolved in calories per mole at any particular composition. At low temperatures, 0–80°, this heat rises slowly with the hydrogen content from an initial value of 6000 at small content of hydrogen, to a value of about 8860 along the horizontal isotherms and reaches values about 9740 for dilution of the second unsaturated solution. The integrated values for $-\Delta H$, in calories per mole of hydrogen, are 8780 at 0°, 8700 at 30° and 8450 at 80°. Mond, Ramsay and Shields[18] measured the heat evolved when hydrogen at about 22° and one atmosphere was run into an ice calorimeter containing palladium. The heat effect per gram of hydrogen increased only very slightly with hydrogen content, was assumed to be constant and the best average value was given as 4644 calories. Per mole this would be 9362. The corresponding $-\Delta H$ for the reaction at one atmosphere and 0° we find to be 9210 calories per mole.[19]

The change of state, however, is indefinite as regards the number and masses (possibly the kinds) of the phases present, since they appear not to have been in equilibrium. Doubtless some of the second unsaturated solution was formed, so that the mean heat per mole should lie between our figures 8860 and 9740, as in fact it does.

Our calculated heats depend on the smoothing used for calculating values in Table I. When the pressures are smoothed, using the improbable assumption that log $p$ is linear with $1/T$, the final result 8780 will be about 5% lower.

## Summary and Conclusions

The equilibrium between palladium and hydrogen has been reinvestigated. It was found possible to bring the system into equilibrium by removing an excess of hydrogen from the gas phase, producing a deficit, thereafter heating the system a short time to about 360° and finally restoring the original temperature. Once the system has been brought to equilibrium in this way, hydrogen can be driven off by short heating to about 360° and be returned to the solids reversibly, although it was not found possible by isothermal operation to remove hydrogen and to replace it with fresh hydrogen.

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[17] Planck, "Thermodynamics," trans. by Ogg. Longmans, Green and Co., New York, 1917, p. 197.

[18] Mond, Ramsay and Shields, *Phil. Trans. Roy. Soc.*, **191A**, 105 (1898).

[19] By subtracting 22, $C_p = 151$. The pressure correction is negligible.

The pressure along the horizontal isotherm at 0° measured in this way was the same as that determined without heating along the first part of the horizontal isotherm.

The conclusion was drawn that this method of securing equilibrium is legitimate and the method was used to determine isotherms at 0°, 30°, 80°, 160° and 180°. Two palladium preparations, reduced to the black metallic state in different ways, were found to give identical isotherms at 0°.

The data are presented in tables and graphs. The graphs show two solid solutions. The saturated solution richer in hydrogen has practically the composition of $Pd_2H$ at 80°, 160° and 180°, but at lower temperatures contains a progressively greater excess of hydrogen.

It is concluded that a hydride, probably best written $Pd_4H_2$, exists which separates practically pure at high temperatures.

Planck's formula for the differential heat of evaporation is used to calculate the decrease in heat content for the formation of (decomposed) hydride. Applied at 0°, 30° and 80°, we find, respectively, 8780, 8700 and 8450 calories per mole of hydrogen. No close check with direct calorimetric data can be obtained, probably because of uncertainty as to the changes of state in the direct calorimetry.

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# THE MILNER AND DEBYE THEORIES OF STRONG ELECTROLYTES

by

George Scatchard

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# *The Milner and Debye Theories of Strong Electrolytes.*

*By* GEORGE SCATCHARD.

(Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 178.)

IN a recent paper of this Journal, Pike & Nonhebel and Nonhebel & Hartley [‡] have published comparisons of the Milner and Debye theories, with conclusions very unfavourable to the latter. On account of the emphasis now being placed upon solutions of strong electrolytes, it seems desirable to show that the experiments of these authors do not necessarily lead to their conclusions.

Since both of these theories explain the deviations from the laws of ideal solutions, their exact forms depend upon the definition of the ideal solution. If this is defined as one in which the activity of each component is proportional to its mole fraction, the equation of Debye and Hückel becomes

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[‡] Pike & Nonhebel, Phil. Mag. vol. l. p. 723 (1925); Nonhebel & Hartley, *ibid.* p. 729.

$$-\log \gamma = \frac{A\sqrt{2c}}{1+\alpha\sqrt{2c}} - B2c + \log(1+0{\cdot}002mw_1), . \quad (1)$$

in which $\gamma$ is the ratio of the activity, $a$, to the molality, $m$, in moles of electrolyte per kilogram solvent; $c$ is the concentration in moles per litre; for a uni-univalent electrolyte at 25°, A is equal to $249{\cdot}4/D^{\frac{3}{2}}$ ($D$ = dielectric constant of solvent); in the same case $\alpha$ equals $2{\cdot}06\times 10^8 b/D^{\frac{1}{2}}$ ($b$ = mean diameter of collision sphere of the ions, in centimetres); B is a complicated function of the temperature, ionic size, dielectric constant of the solvent and rate of change of the dielectric constant with changing electrolyte concentration.

Equation (1) contains two constants, $\alpha$ and B, which can be determined only approximately by independent measurements. Moreover, expansion of the first term on the right-hand side in a power series of $c$ shows that the two are differentiated only in the coefficients of the three-halves and higher powers of $c$. So the equation may be simplified in dilute solutions. In the case of solvents of low dielectric constants, such as the alcohols, the term $B2c$ may be omitted, and the only effect will be to make the value of $b$ calculated from $\alpha$ somewhat too large. In more dilute solutions the equation approaches

$$-\log f = A\sqrt{2c} - B'c, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which $f = a/c$ and $B'$ is a new constant. At zero concentration the equation approaches

$$-\log f = A\sqrt{2c}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The formula of Milner cannot be expressed analytically. It gives the same values for all electrolytes of the same valence type, and values which do not differ very much from two-thirds those calculated from equation (3).

Nonhebel and Hartley compare the two theories with the experimental measurements of electromotive force of hydrochloric acid cells in water, ethyl alcohol, and methyl alcohol. They find that the Milner formula gives approximate agreement and that the Debye theory is much less satisfactory. In testing the Debye theory, however, they use equations (2) and (3) instead of equation (1). I have discussed elsewhere * the comparison of the complete theory of Debye and Hückel with the experimental measurements in water, in ethyl alcohol, and in their mixtures, and found the agreement to be excellent. So the present discussion may be limited to the new measurements in methyl-alcohol solutions. Attention should be called, however, to the solubility measurements of Brönsted and La Mer †, which agree very closely with the Debye theory, but not at all with that of Milner.

Nonhebel and Hartley first test the two theories by the constancy of the quantity $E_0$, which may be defined by the equation

$$E_0 = E + 0{\cdot}1183\,(\log c + \log f) = E - 0{\cdot}0123$$
$$+ 0{\cdot}1183\,(\log m + \log \gamma), \quad . \quad . \quad . \quad . \quad (4)$$

in which $-0{\cdot}0123$ is equal to $0{\cdot}1183\,(\log c - \log m)$ for methyl alcohol at 25°, and E is the measured electromotive force. In their test of the Debye theory, $\log f$ is determined from equation (3). They later compare $f$, calculated by equation (2), with the values computed from the experimental measurements and the value of $E_0$ determined by the use of Milner's formula. Both tests are inconclusive, because Debye's theory is not represented by either of these equations through the concentration range of the experimental measurements; the second method also uses a quantity determined by the use of one theory in the test of another theory incompatible with the first.

The combination of equations (1) and (4), with insertion of the proper values for methyl alcohol ($D = 30{\cdot}2$), gives

$$E_0 = E - 0{\cdot}0123 + 0{\cdot}1183\,[\log m - \log(1 + 0{\cdot}064\,m)]$$
$$- \frac{0{\cdot}1767\sqrt{2c}}{1 + \alpha\sqrt{2c}} + B2c. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The values of $c$ were computed by me from the approximate equation

$$c = \frac{m}{1{\cdot}2716 + 0{\cdot}02m}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

If B be given the value zero, which is justifiable in the concentration range studied, the experimental data are best fitted with $\alpha = 1{\cdot}74$. Table I. and fig. 1 give the test of equation (5) and the comparison with the Milner formula.

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* Journ. Am. Chem. Soc. xlvii. p. 2098 (1925).

† Bronsted & La Mer, Journ. Am. Chem. Soc. xlvi. p. 555 (1924).

In Table I. the first column gives the values of $m$; the second the values of $E_0$ computed by Nonhebel and Hartley with Milner's formula; the third the deviations of the values of the second column from the value of $E_0$ accepted by these authors; the fourth column contains the values of $E_0$ computed from equation (5); and the fifth gives the deviations of the values of the fourth column from their average, $-0{\cdot}0226$ volt. Fig. 1 shows the same results graphically. It differs from fig. 2 of Nonhebel and Hartley in that it extends to higher concentrations and in that the ordinates are shown on a ten times larger scale. No attempt is made to draw curves through the points. Instead, the two accepted values of $E_0$ are represented by horizontal dotted lines.

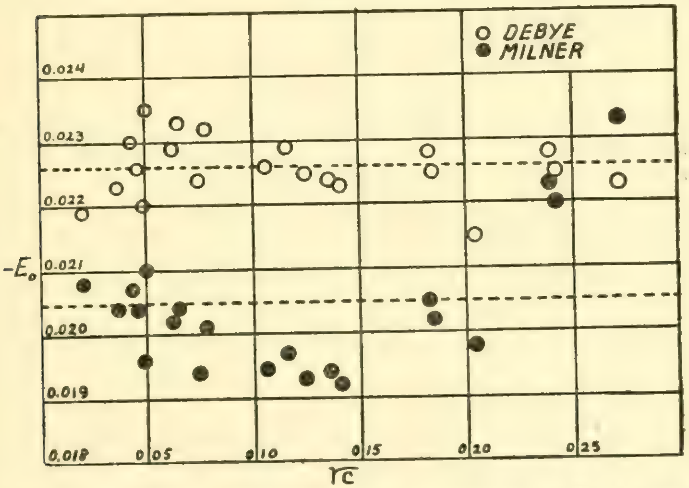
### TABLE I.

Electromotive Force in Methyl Alcoholic Hydrochloric Acid at 25°.

| | MILNER. | | DEBYE. | |
|---|---|---|---|---|
| $m$. | $-E_0$. | $-E_0-0{\cdot}0205$. | $-E_0$. | $-E_0-0{\cdot}0226$. |
| 0·0004955 | 0·0208 | +0·0003 | 0·0219 | −0·0007 |
| 0·001652 | 0·0204 | −0·0001 | 0·0223 | −0·0003 |
| 0·002363 | 0·0207 | +0·0002 | 0·0230 | +0·0004 |
| 0·002683 | 0·0204 | −0·0001 | 0·0226 | 0·0000 |
| 0·002980 | 0·0196 | −0·0009 | 0·0220 | −0·0006 |
| 0·003161 | 0·0210 | +0·0005 | 0·0235 | +0·0009 |
| 0·004939 | 0·0202 | −0·0003 | 0·0229 | +0·0003 |
| 0·005425 | 0·0204 | −0·0001 | 0·0233 | +0·0007 |
| 0·007113 | 0·0194 | −0·0011 | 0·0224 | −0·0002 |
| 0·009857 | 0·0201 | −0·0004 | 0·0232 | +0·0006 |
| 0·01444 | 0·0194 | −0·0011 | 0·0226 | 0·0000 |
| 0·01722 | 0·0197 | −0·0008 | 0·0229 | +0·0003 |
| 0·01986 | 0·0193 | −0·0012 | 0·0225 | −0·0001 |
| 0·02363 | 0·0194 | −0·0011 | 0·0224 | −0·0002 |
| 0·02549 | 0·0192 | −0·0013 | 0·0223 | −0·0003 |
| 0·04261 | 0·0205 | 0·0000 | 0·0228 | +0·0002 |
| 0·04356 | 0·0202 | −0·0003 | 0·0225 | −0·0001 |
| 0·05312 | 0·0198 | −0·0007 | 0·0215 | −0·0011 |
| 0·07332 | 0·0223 | +0·0018 | 0·0228 | +0·0002 |
| 0·07333 | 0·0223 | +0·0018 | 0·0228 | +0·0002 |
| 0·07507 | 0·0220 | +0·0015 | 0·0225 | −0·0001 |
| 0·09467 | 0·0233 | +0·0028 | 0·0223 | −0·0003 |
| 0·1155 | ... | ... | 0·0229 | +0·0003 |
| 0·4802 | ... | ... | 0·0234 | +0·0008 |
| 0·5574 | ... | ... | 0·0224 | −0·0002 |

It is obvious from either the table or the figure that the complete Debye equation gives an $E_0$ value more constant than the Milner formula. Not only is the average deviation smaller, even up to 0·04 M, but there is no trend in the deviations, and the equation holds equally well up to the highest concentrations measured, which are ten times those at which the Milner formula begins to deviate seriously. It is also apparent that $E_0$ calculated from the Debye equation is as constant as the consistency of the experimental data warrants, and $-0{\cdot}0226$ volt may be taken as the most probable value for $E_0$. It may be concluded that these measurements, considering the enormous difficulties of precise measurement in very dilute alcoholic hydrochloric acid, offer very good confirmation of the Debye theory.

Fig. 1.



From the value of 1·74 for $\alpha$, the mean diameter of the collision spheres is $4{\cdot}65 \times 10^{-8}$ cm. Other values for hydrogen chloride are: $4{\cdot}05 \times 10^{-8}$ in water, $4{\cdot}06 \times 10^{-8}$ in 50 mole per cent. ethyl alcohol, and $4{\cdot}57 \times 10^{-8}$ in ethyl alcohol *. Since the value in methyl alcohol is somewhat too large on account of the change in dielectric constant being neglected, the agreement is very satisfactory.

I have shown how the radius of the electrification sphere can be calculated from the $E_0$ values in different solvents with the assumption that all the deviation from ideality is due to the electrical work. To account for the behaviour

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* Scatchard, *loc. cit.*

of hydrochloric acid in alcohol-water mixture, it was suggested that this size might change from 5 to $4 \times 10^{-8}$ cm. between 50 and 95 mole per cent. alcohol. From these measurements in methyl alcohol and those of Danner in ethyl alcohol a value of $3{\cdot}0 \times 10^{-8}$ may be calculated. The calculation is not very accurate, because the difference in dielectric constants and between electrode potentials in terms of mole fractions are both very small. Since any change in size is to be attributed largely to the reaction $H_2C^+ = H^+ + H_2O$, the change between 95 and 100 mole per cent. might well be as great as that between 50 and 95 mole per cent. Considering the breadth of the assumptions and the large effect of a small experimental error the agreement is quite satisfactory.

## *The Milner Formula.*

Although Milner and Debye start with the same fundamental theorems of electrostatics and statistical mechanics, the results they obtain do not agree quantitatively. Milner states that "It may be shown that, as an approximation, and when $h$ [*] is very small" the value of the virial of the ions is 1·253, or $\sqrt{\frac{\pi}{2}}$, that given by the limiting law of Debye, equation (3). Yet when $h$ has the value corresponding to a concentration of 0·0001 M for a uni-univalent electrolyte in water at 0°, his virial is only 0·734 that of the equation (3), and the ratio decreases only to 0·656 in 0·2 M solution [†]. Most of this discrepancy may be attributed to inaccuracy in the Milner results. Milner himself continually refers to them as approximate. It seems probable that all his values are obtained by interpolation from the three values given in his first paper [‡]. These results are obtained by graphic extrapolation from fifteen to infinity. To decrease substantially the range of extrapolation would require an amount of computation several thousand times that performed by Milner. It is worth while then to re-examine his method of extrapolation.

Since Milner's tables include data for only one of the three pairs of curves, his curves cannot be replotted accurately. Fig. 2, however, was obtained photostatically without serious distortion. To quote Milner again, "The extrapolation of these curves to the axis is certainly a rather violent one, but it may be done with some confidence by observing the following points:—(1) The first curve must be everywhere below the limit and the second one everywhere above it; (2) the two curves must extrapolate to the same point on the axis; (3) from the fact that the virial of the ions external to the second arrangement is zero, it may be inferred that the second curve for large values of $m$ * approaches the limit much more closely than the first one, and that it probably tends to become parallel to the axis as $m^{-\frac{1}{3}}$ becomes zero."

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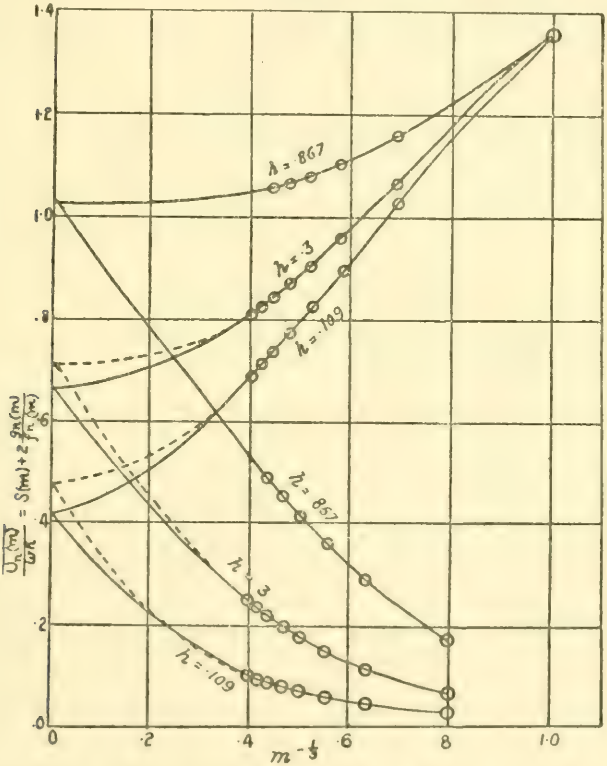
[*] $h$ is a function of the ionic charge, the dielectric constant of the solvent, the temperature, and the concentration. By Milner's theory the virial is equal to $RTh f(h)$.

[†] A. A. Noyes, Journ. Am. Chem. Soc. xlvi. p. 1080 (1924).

[‡] Milner, Phil. Mag. xxiii. p. 551 (1912).

Fig. 2.



Inspection of fig. 2 shows that the dotted lines fulfil these conditions, especially the third, even better than do the full lines which represent Milner's extrapolation. The

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* $m$ is the number of ions whose effect on the virial is counted

lowest pair might equally well be extrapolated to a still higher value. The results of the two extrapolations and the value of the Debye limiting law, equation (3), are given in Table II. The last two columns show the corresponding concentration of a uni-univalent electrolyte in water at 0° and in methyl alcohol at 25°. The most important conclusion to be drawn is that the Milner theory does not lead necessarily to the Milner formula, but may equally well give higher values for the slope. The values in the third column of Table II., which are shown in fig. 2 to be consistent with the Milner theory, were computed from the equation

$$f(h) = \frac{\sqrt{3h}}{1+0{\cdot}35\sqrt{3h}}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which at small concentrations must approach the Debye limiting law, which corresponds to $f(h) = \sqrt{3h}$.

TABLE II.

$f(h)$ of Milner's Theory.

| $h$. | $f(h)$. Milner. | $f(h)$. Eq. 4. | $f(h)$. Debye ($\sqrt{3h}$). | $C_{H_2O}$. | $C_{MeOH}$. |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0·0 | 0·0 |
| 0·109 | 0·42 | 0·48 | 0·57 | 0·0007 | 0·00004 |
| 0·3 | 0·66 | 0·71 | 0·95 | 0·015 | 0·00085 |
| 0·867 * | 1·03 | 1·03 | 1·61 | 0·362 | 0·0206 |

There must, however, be a discrepancy between the results of Milner and the limiting law of Debye at finite concentrations, a discrepancy which increases with increasing concentration. There are two possible explanations: both methods give only approximations of the virial, the approximations may not be exactly the same; both methods consider the size of the ions in the early stages but ignore the size later, and the exact stage at which the size of the ions is ignored may influence the effect so that, relative to equation (3), the Milner theory may make a partial correction for ionic size. It would be an extremely tedious task to settle these points for the Milner theory. The Debye theory, on the other hand, is so direct in its development that the approximation may be improved at any time by including more terms in the series used to approximate the

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* To quote Milner again; "This value of $h$ is so large that the expression for the virial obtained in this paper would no longer be valid."

Boltzmann equation. It already gives a method for taking into account the size of the ions, and may readily be made more accurate in this respect whenever there is discovered a law for the repulsive forces between atoms more accurate than the rigid-sphere assumption.

## *The Determination of Free Energies from the Mutual Potential Energies of the Ions.*

Pike and Nonhebel criticize the method of calculating the free energy from the mutual potential energy of the ions by an equation of the Gibbs-Helmholtz type, and claim that it cannot lead to quantitative results. Much of their argument is an attack on an equation of Debye and Hückel, given on page 725 between equations (10) and (11). This equation does not follow from the Debye theory without additional assumptions, and it is thermodynamically incompatible with the Debye theory for the free energy of the solutions. Although the equation is undoubtedly incorrect, that fact cannot effect the validity of the Debye theory.

Gross and Halpern [*] have given a justification of the method used by Milner and by Debye and Hückel, in which the relation between the mutual potential energy of the ions and the free energy of the solution is obtained by using the *partial* derivative of the free energy with respect to the temperature. They have also shown that the relation between the total internal energy of the solution and the free energy, for which the thermodynamics requires the *total* derivative with respect to the temperature, shows at least approximate agreement between the Debye theory and thermal measurements if the size of the ions varies slightly with the temperature.

Another confirmation of the exactness of this method is obtained from the fact that the same result has been obtained by three other methods, none of which depend on an integration with respect to the temperature. The first of these, used by Milner and by Nonhebel and Hartley, is to take the osmotic pressure as equal to the virial. The second, given by Noyes [†], calculates the vapour-pressure of the ions from kinetic theory. These two are applicable only in dilute solutions. The third method [‡] makes use of the difference in electrical work of charging the ions reversibly in the solution in question and in an infinitely dilute solution It may be applied to solutions of any concentration.

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[*] Gross & Halpern, *Physikalische Zeitschrift*, xxvi. p. 403 (1925).

[†] Noyes, *loc. cit.*

[‡] Debye, *Physikalische Zeitschrift*, xxv. p. 97 (1924).

Gross and Halpern * object to this last derivation on the grounds that the potential of any individual ion oscillates rapidly about the mean potential. This objection could be met by the invention of a device which would prevent the discharging of an ion and permit its charging only when its potential and charge each differ from the average by less than some infinitesimal amount. Such a device would increase the order of infinity of the time of the charging process, but that is unimportant in a purely theoretical process, in which the question of practical realizability is irrelevant.

The application of thermodynamic criteria to this step of the derivation is entirely beside the point, since one quantity involved—the mutual potential energy of the ions—cannot be represented by any of the ordinary thermodynamic equations; for these equations are incapable of dividing energy between the components of a phase. The final results may be tested thermodynamically by the application of the ordinary equations. In all tests so far made of the Debye theory, an agreement at least approximate has been found.

Cambridge, Massachusetts.

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* Gross & Halpern, *loc. cit.*

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# PUBLICATIONS

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# AN EXPERIMENTAL STUDY OF THE PISTON PRESSURE GAGE TO SIX HUNDRED ATMOSPHERES

by

Frederick G. Keyes and Jane Dewey

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## INTRODUCTION

The "dead weight" piston gage has come into extended use during the past twenty years as an accurate pressure measuring instrument. The gage consists essentially of a uniform cylindrical piston fitting suitably into a cylinder and supporting, at the exposed end, a known weight which balances the hydrostatic pressure exerted by a pressure transmitting fluid on the lower surface of the piston.

It is evident that the weight required to equilibrate a given hydrostatic pressure will be a function of the area of the piston. For a piston closely fitting its cylinder, the weight required is assumed to be proportional to the mean area of piston and cylinder. In practice, however, it is a difficult task to determine the area or rather diameter of the cylinder with sufficient accuracy and recourse can be made to calibration of the gage against a pressure standard. The latter ultimately must of course be interpreted in terms of the pressure exerted by a column of mercury. In this laboratory the mercury-in-glass column is 900 cm in length while prior to 1916 a column 1280 cm long was available. All pressure measurements which have hitherto been made in this laboratory are referred directly to a calibration of the gage used, against a mercury column and the gage "constant" thereby determined has been employed to extrapolate to pressures as high as 2000 atm.

The uncertainty which may attend this long extrapolation has been a matter of concern and plans have from time to time been discussed in detail for erecting a column in a suitable mine shaft. The expense, however, of carrying out the project is so considerable that each year has seen the project postponed. The decision has been made therefore to employ in principle the method used by Holborn and Schultze[1] whereby use is made of a column of moderate length with two gages having pistons of substantially equal diameter.

The Holborn and Schultze apparatus consists of a column of about 1700 cm in length, at the upper end of which a gage is placed while a second and similar gage is installed at the lower end of the column.

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* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 179.

[1] Holborn and Schultze, Ann. d. Phys., *47*, p. 1095; 1915.

After each gage had been compared with the open column, the pressure at the upper gage may be adjusted to equal one column length, thereby producing a pressure of two column lengths at the lower gage. By continued interchanges of the gages, comparisons of the gage "constants" may be made to any desired pressure within the limits of pressure for which the columns and gages are designed to operate.

The foregoing principle has been applied to obtain the measurements herein recorded. In our application certain modifications in the details of the disposition of the apparatus have been employed, such for example as installing both test gages at the lower level of the column and making the exchange of gages by suitable manipulation of stopcocks rather than physically interchanging the top and lower gages.

A mercury-in-glass column of 900 cm length was first employed to obtain the low pressure gage "constants." Each gage was subsequently used to determine the length of a mercury column in a steel tube of very nearly the same length as the mercury-in-glass column. The steel column was water jacketed and pressure transmission from the upper end of the column to the second gage was secured by means of oil contained in a tube inclosed within the same water jacket as the mercury column.

The method of detecting pressure equilibrium[2,3] was essentially the same as that in use in this laboratory for pressure measurements for the past fifteen years. This electrical method enabled the pressure comparisons to be made with speed and great accuracy.

Some years ago Professor Beattie made some comparisons of a piston gage with the 900 cm mercury-in-glass column employing oils of different viscosity. The "constant" obtained was independent of the oil viscosity within the limits of error of the comparison which was about 1 part in 20,000, thus confirming what would be inferred on theoretical grounds.[4] The pressure range, however, was small (12atm.)

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[2] Keyes and Brownlee, Thermodynamic Properties of Ammonia, Wiley & Sons, p. 11; 1916.

[3] Keyes, Joubert and Smith, Jour. Math. & Phys., M.I.T., p. 195; 1922.

[4] For the steady motion of a cylindrical shell of incompressible fluid moving upward in the direction of the $z$ axis the usual hydrodynamical equation is:

$$\frac{\mu}{r}\frac{\partial}{\partial r}\left(r\frac{\partial w}{\partial r}\right) = \frac{\partial p}{\partial z} = \text{constant}$$

where $\mu$ is the coefficient of viscosity, $w$ the velocity along the direction of the $z$ axis, $p$ the pressure per unit area, and $r$ the radius of the cylinder. The space between the piston and cylinder for the case of exact coincidence of the two axes may be designated $(a-b)=\sigma$ where and it might be desirable to extend this investigation to higher pressures using the present calibration system. It should be emphasized that the theory of the effect of the escaping oil indicates independence of the gage indications from viscosity variations for an incompressible oil. In the present paper the same oil was used throughout the measurements.

The ideal piston and cylinder, namely one absolutely rigid and inexpansible with heat, would disclose a "constant" on comparison with the mercury column which would be independent of the pressure. The gages employed in the present work consist of a hardened piston and cylinder, the former being ground and lapped to fit the lapped hole of the cylinder. The primary purpose of this investigation was to determine by experiment the effect of the stress system set up in the piston and cylinder on the effective area under the usual conditions of use. The elasticity theory has already been envoked to indicate the nature of the effect which distortion of the piston and cylinder may have upon the effective area of the piston. Thus the effective area of the 0.159 cm piston used by Bridgman[5] was calculated to change due to the stress system by $1.8\times10^{-7}\times p$ kgm. The effect would require a correction of about 1/500 in the pressure at 10000 kgm.

Michels[6,7] has recently elaborated in detail the theory of the Schäffer and Budenberg differential piston gage based on the usual elasticity theory and made some measurements of the effective area of a differential piston of the Schäffer and Budenberg type. The latter measure-

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$a$ and $b$ are the radii of cylinder and piston respectively. If no "slip" occurs at the solid boundaries $\partial w/\partial r$ is zero as usually assumed. Integration of the equation above gives

$$\mu\frac{\partial w}{\partial r}=\frac{\sigma}{2}\frac{\partial p}{\partial z}\frac{a+b}{r}$$

Since $a$ is nearly equal to $b$, $(a+b)/r$ may be taken as very nearly 2 and the total force on the cylindrical surface perpendicular to $r$ becomes:

$$F=\pi a\sigma\frac{\partial p}{\partial z}l=\pi a\sigma(p_1-p_0)$$

This shows that the force due to the escaping oil and tending to lift the piston is independent of the viscosity of the oil and remains an invariable fraction of the pressure measured. The equation is in agreement with Michel's which was obtained by a different method involving the same assumptions.

If compressibility of the liquid is allowed for, an equation of state of the liquid must be assumed. The result obtained above, however, would be but slightly modified.

[5] P. W. Bridgman, Proc. Am. Acad., *47*, p. 321; 1911.

[6] A. Michels, Ann. der Phys., *72*, p. 285; 1923.

[7] A. Michels, Ann. der Phys., *73*, p. 577; 1924.

ments made use of a closed hydrogen manometer provided with electrical contacts sealed into a hydrogen closed manometer tube whereby the same setting could be very exactly reproduced. By balancing the pressure corresponding to the hydrogen manometer setting first against the gage and second against the gage plus a 500 cm mercury column, it was possible to compute the gage constant at the pressures corresponding to the fixed contacts of the hydrogen manometer. Measurements were carried out in this manner from about 40 atm. to 178 atm. There was no detectable trend in the effective areas measured. The consistency of the observations on the other hand was about 1 in 3000. Application of the theory to the particular piston used by Michels indicated that at the highest pressure actually measured (178 atm.) the correction for distortion would be much less than 1 in 3000.

## DESCRIPTION OF APPARATUS

The gages used in this investigation are similar in design to those previously in use in this laboratory with the exception of some improvements in the design of the piston oscillating mechanism and the design of the piston-cylinder. The former produces a uniform motion in both directions whereas formerly the motion was non-uniform. The piston-cylinder design is such as to use cylinders (of fixed external dimensions) carrying different diameter pistons and thus the five standard sizes of piston in use for general pressure measurements can be employed in the same piston-cylinder block. The range of pressures which can be measured extends from several atm. to about 2000 atm.

In the reproduction of the photograph Fig. 1, there is shown the motor, gage block and gage complete except for the scale pan. The piston and cylinder is not visible being hidden by a brass cylindrical support surrounding the nut which holds the cylinder into the block. Attached to the upper portion of the piston is an arm extending at right angles which is moved back and forth through an angle of 30° by means of a fork, bearing hardened rollers and oscillated by the motor. The oscillation rate is 30 per minute. The cross beam from which the scale pan is provided with a ball bearing at the point where it is supported on the piston.

The effect of temperature on the effective diameter requires attention in the present work since a variation of 1° produces a change in effective piston diameter in amount $2.4\times10^{-5}$ or 1 part in 42000. The variations in operating temperatures of the gages are large enough to make the application of this correction necessary in view of the reproducibility of the comparisons which will be presented.

Two types of scale pan are used with the gages, the larger of which weighs somewhat less than 20 kilos and is used with a total load of 300 kilos. The lighter pan of aluminum is used for the measurements of pressure to 20 atm. and is employed in calibrating the gage against the mercury in glass column as well as in the present work for ascertaining the length of the mercury in steel column. Fig. 2 shows the disposition of the gates with scale pans, oil injector, electrical contact, detecting apparatus, and stopcocks used for interchanging the roll of the gages from top to bottom of the mercury in steel column.

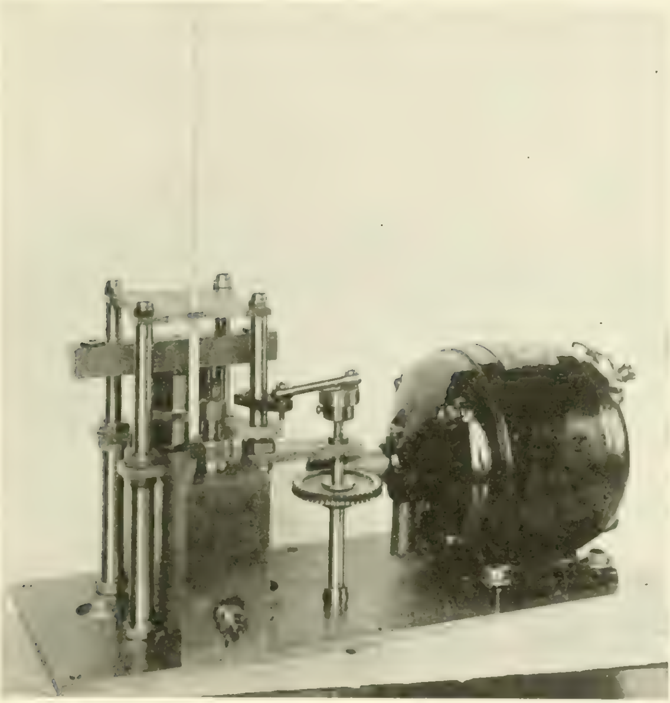

FIG. 1. *Pressure gage.*

Two sizes of piston were used in the present investigation referred to as No. 8 and No. 9 large, and No. 8 and No. 9 small. The former had an area of about four fold the latter. Each of these pistons was calibrated against the mercury in glass column. The constants of the gages (reciprocal of effective area divided by 1/10th the density of mercury) will be expressed as the number of grams weight which enables the piston at 30° to support 1 mm of mercury at the temperature of melting ice and corresponding to a gravitational constant of 980.397.*

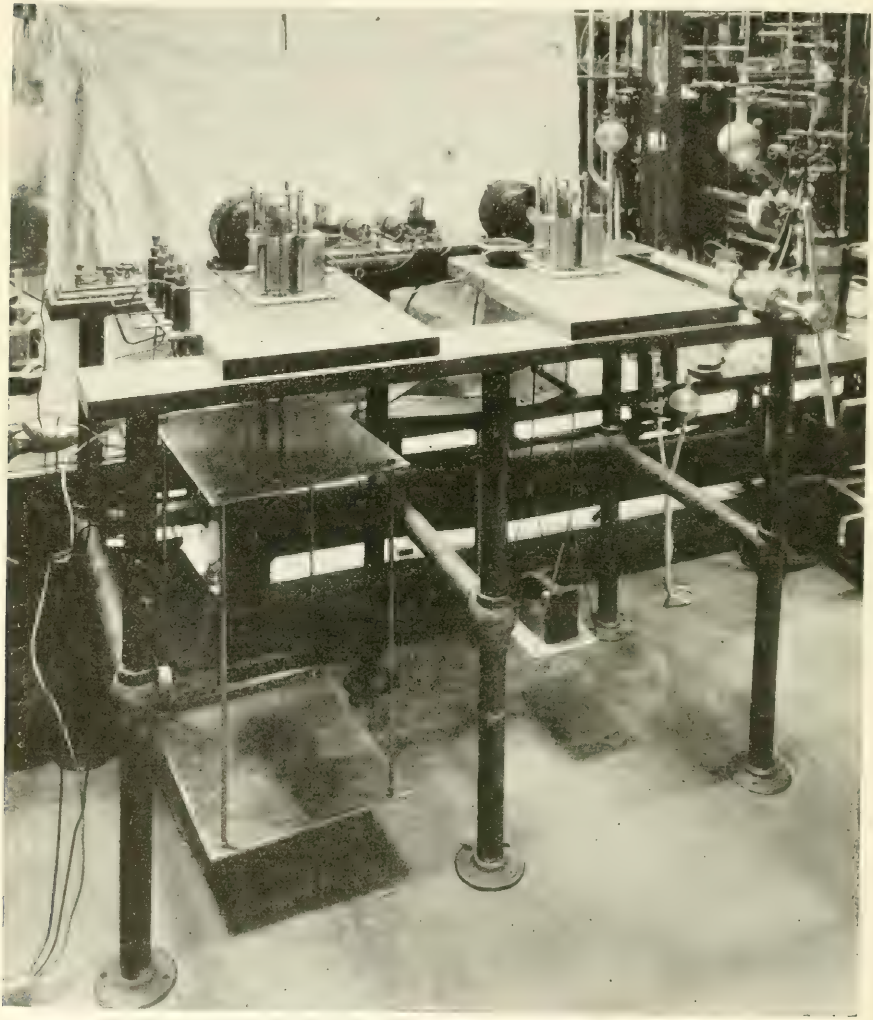

FIG. 2. *Actual arrangement of gages and stopcocks.*

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* This is the value of the constant at this laboratory. Since in this paper relative values are alone in question, reduction was not made to the international value used for pressures (980.665).

## THE MERCURY-IN-GLASS COLUMN

The glass column 900 cm in length was contained and supported in a vertical rectangular shaped trough, the front of which could be covered with card board covers to assist in maintaining the temperature constant. Thermometers were placed in proximity to the column and enabled the mean temperature of the column to be ascertained. The column could be filled to any desired height by injecting oil by means of a Cailletet pump into a closed vessel containing mercury from which a tube lead to the lower end of the glass mercury column. The gages could be connected by means of an oil lead to the short arm of the manometer, which was provided with a platinum contact. The disposition of apparatus was in fact similar in every respect to that described and illustrated some years ago[8] with the exception that the electrical contact equilibrium indicator was sealed directly into the glass of the manometer short arm.

The height of the column was measured by a standard steel tape stretched under a load of 6 kilos and calibrated against a meter bar which in turn had been compared at the United States Bureau of Standards. All large weights used had been compared with the Massachusetts State House Standards[9] while the smaller set was compared with a one kilo set of weights calibrated at the United States Bureau of Standards. All results of the column comparisons are reduced to gage temperature 30° and the results presented in table 1.

TABLE 1. *Gage constants at 30° from comparisons made with a mercury column 900 cm in length.*

| | Size | Gage constant |
|---|---|---|
| Piston number 8 | large | 0.499370 mm per g. $\pm 0.15 \times 10^{-4}$ |
| " " 9 | " | 0.499405 mm per g. $\pm 0.24 \times 10^{-4}$ |
| " " 8 | small | 1.99637 mm per g. $\pm 1.0 \times 10^{-4}$ |
| " " 9 | " | 1.99479 mm per g. $\pm 1.4 \times 10^{-4}$ |

It will be noted that the average deviation from the mean for No. 8 and No. 9 large piston is about 1 part in 25000 and that the effective areas are within 1 in 14000 of one another. The smaller piston No. 8 and No. 9 are not so closely of the same effective area.

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[8] The Thermodynamic Properties of Ammonia. John Wiley & Sons, p. 11, 1916.

[9] We take pleasure in expressing our great obligation for the painstaking aid given us and the courtesy shown by Mr. Francis Meredith, Director of Standards of the State of Massachusetts.

## THE MERCURY IN STEEL COLUMN

To withstand the pressures contemplated in the comparison of the gage indications at higher pressures it was necessary to employ a mercury-in-steel column. The details of construction are represented in Fig. 3. The length of the column was about the same (875 cm as compared with 900 cm) as the glass column. The bore of the column was 1 cm with a wall thickness of 0.476 cm. In the figure the steel column is designated *A* and the end is threaded and formed to make the connecting joint directly on the tube. The block *B* receives the latter through which it communicates to the manometer short arm; a Cailletet pump used to inject oil which forces mercury into the column, and a piston mercury injector, *I*, for fine adjustment of column height. Each end of the column is provided with a mercury-oil contact needle $R_1$ and $R_2$ which carries an oil connection leading to the stopcocks. Connection is finally made from the latter to the gages.

The electrically insulated mercury-oil contact needles are connected with an electrical device for giving visual indication when contact is made or broken at the mercury-oil junction. The electrical apparatus consists of a relay operating on 0.002 amp. used to connect the circuit to a four volt flash light bulb as illustrated in the drawing. With the device sketched a very minute current passes at the needle mercury miniscus. The light comes on promptly when the contact is broken and extinguishes when contact is made. This electrical circuit is the result of a sustained effort to improve the contacting device and is very satisfactory. It has been found essential to have as small a current as possible pass between the needle and mercury otherwise emulsification of the mercury in the oil takes place disturbing the distinctness and reproducibility of the contact.

The drawing aims to make clear that the manipulation of the stopcocks $S_1$, $S_2$, $S_3$, $S_4$, permits either gage to be connected to the top or bottom of the column at will.

The top of the column is connected to the gage by means of the tube *C* of 0.7 cm internal diameter. The oil used was a clear grit free "vacuum" oil whose density was found to be $0.9083+0.000534t$ and compressibility $53.1\times10^{-6}$ cc per atm. per cc at 25°.

The two gages $G_8$ and $G_9$ are shown in end view together with the oil injector connected to one of the gages. Each gage was provided with an oil injector in practice in order that oil could be supplied to make up for leak and to displace the pistons as required.

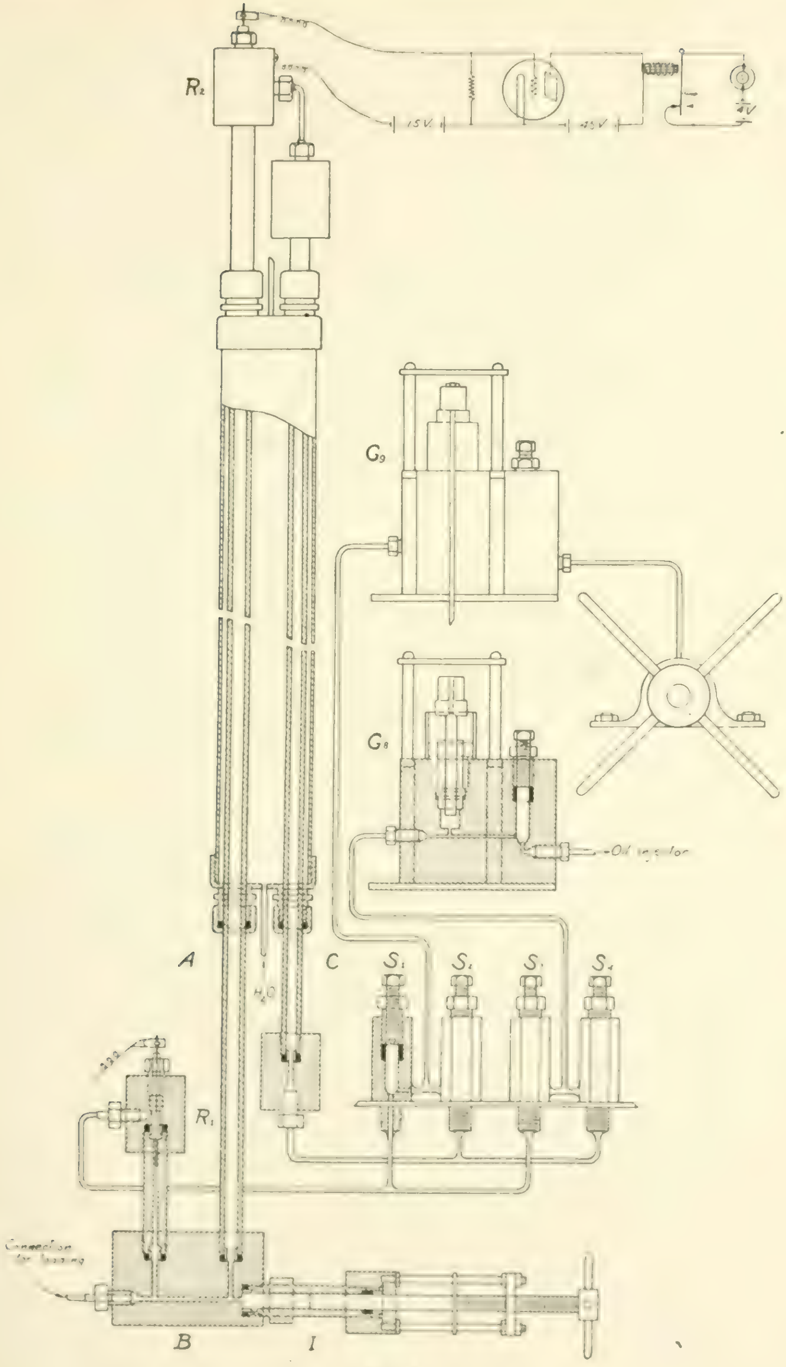
$R_2$
15 V.
45 V
4V
$G_9$
$G_8$
Oil injector
A
C
$H_2O$
$S_1$
$S_2$
$S_3$
$S_4$
$R_1$
Connection
B
I

FIG. 3.

Both the mercury-steel and oil columns were inclosed in the same brass water jacket consisting of a 7.5 cm brass tube lagged externally with a standard pipe covering. It was found preferable to circulate water in a closed circuit by means of a gear pump rather than allow the water from the mains to flow through the jacket. The latter procedure produced a temperature difference between top and bottom of the column of from 2 to 4 degrees whereas the closed circuit arrangement lead to a difference never greater than one degree. The actual temperatures along the column were read by means of three thermometers placed at the bottom, middle and top. The bulbs of these thermometers rested between the mercury tube and the oil tube. The top of the column was exposed for a short distance but it was lagged with hair felt and the temperature obtained by means of two thermometers placed along the exposed portion of the column.

The loading of the column with mercury was accomplished by first exhausting the column and subsequently admitting mercury from the mercury reservoir and pumping in the mercury by means of the Cailletet pump. When approximately the correct amount of mercury had been introduced additional mercury was injected by means of the mercury injector *I*. By means of the latter the mercury could be adjusted to very exact contact with the insulated needles at top and bottom and thus a fixed length of mercury could be made available at all times.

## CORRECTIONS APPLIED TO THE MERCURY IN STEEL COLUMN

The temperature dilation of the pure mercury and its compressibility must be accurately known to reduce the column lengths of mercury in the steel column to the force per unit area which corresponds to the defined unit of pressure. Reduction was not made to the international pressure unit with respect to gravity since relative pressure values suffice in the present investigation.

In addition to the mercury constants there is required the stretch of the steel column under internal pressure and also the expansivity of the steel with temperature. The constants used in reducing the observations are contained in Table 2.

The length of the steel column between needle points was determined under a slight pressure (1 atm.) exerted at the top of the column. This length as determined by using both the larger pistons was 875.12 cm ±0.09 at 22.8°.

TABLE 2. *Properties of mercury, steel and oil used in reducing column lengths of mercury to standard conditions.*

| | |
|---|---|
| Mean volume expansion of mercury (0–25°) | $1.82\times10^{-4}$ cc per cc |
| Mean linear expansion of steel (0–25°) | $0.1184\times10^{-4}$ cm per cm |
| Compressibility of mercury 22° | $(3.94-1.1\times10^{-4}\,p\,\text{atm.})\times10^{-6}$ cc per cc |
| Young's modulus for steel 20° | $2.2\times10^{6}$ atm. per $\overline{\text{cm}}^2$ |
| Area of steel column section | $2.136$ cm$^2$; bore of column $0.712$ $\overline{\text{cm}}^2$ |
| Density of oil used | $(0.9083–0.00053\,t)$ gm per cc |
| Compressibility of oil used | $53.1\times10^{-6}$ cc per cc per atm. at 25° |

## EXPERIMENTAL RESULTS

The data obtained have been reduced and listed in Table 3 for the larger pistons while the differences between true and indicates pressures are plotted in Fig. 4, for the smaller pistons. The method of obtaining the pressures in column 9, each entry of which corresponds to a certain number of column lengths is as follows. The first entry of column 3 (Table 3) is the pressure exerted by the gage connected to the upper end of the column. This pressure is computed from the total weight applied to the piston using the gage constant determined from the comparisons made with the gage against the mercury-in-glass column. The pressure of the single column lengths appear in column 5. To 1474.7 mm there must be added then 8137.6 mm giving 9612.3 mm (9th column) which is to be compared with the pressure measured by the gage connected to the lower end of the column. The gages are next interchanged without altering the weight applied to the piston which in the former setting was connected to the lower end of the column. Equilibrium is again obtained, the lower gage now indicating a pressure of 17748.2 mm. The mercury column pressure with which this is to be compared is 9612.3 mm (column 9, 1st row) plus an additional length of mercury 8137.5 mm corrected for any difference in pressure exerted by the upper gage as a consequence of a temperature change in

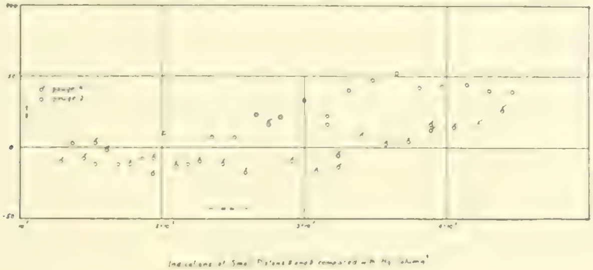

FIG. 4.

the latter from the time it was used to measure a pressure to the time it was used to apply a pressure at the top of the column. This difference is obtainable as the difference between columns 8 and 3 for the same gage. For example the sixth entry shows a pressure of 25890.3 mm exerted at the top of the column by gage 8 at 30° which in entry 5, 8th column, was at a temperature of 27° the difference of 1.7 mm corresponds to the pressure difference arising from the increased area of piston 8 due to 3° rise in temperature. The numbers in column 9 are therefore pressures obtained by successively adding column lengths of mercury to the small initial pressure of 1474.7 mm and the 8th column represents the pressures computed from the gages using the constants obtained in the low pressure comparisons with the glass column. From Table 3 on comparing columns 8 and 9 it will be evident that no particular trend is disclosed and to 160 atm. the effective piston area is not sensibly altered.

Fig. 4 exhibits the reduced data pertaining to the smaller diameter pistons. The initial pressure used corresponds to the limiting pressure to which comparisons were carried in the use of the large pistons. The limit of pressure attained in the comparisons of the small pistons with the mercury column is about 587 atm.

The indication is that a small trend exists in the pressures given by the small pistons of which piston 9 shows the larger trend. The data plotted in Fig. 4 indicates clearly that at the higher pressure range the indications of gage 9 are on average higher than those of gage 8. The mean deviation is however but one part in 10,000 greater than the mercury column pressure.

Without doubt the difference in the indications of the two gages is to be traced to differences in the fit of the pistons in their respective cylinders, although the precise nature of the causes underlying the difference is not known at present. It has already been noted that a piston which fits its cylinder too closely is not reliable in its indications. A test of piston suitability which has been attempted in a preliminary manner is to apply an electric current to the piston and cylinder. It appears that a reliable piston-cylinder always gives perfect insulation of one member from the other during the oscillation, contact being made of course at the reversal of the oscillation. The inference from this fact would be that the piston must be actually "floating" on the oil during the major portion of the time that it is acting as a pressure measuring device.

It is now, so far as known, generally admitted that oscillation of the piston is to be preferred to complete rotation; a conviction of one of the present writers some fifteen years ago. It is now believed, as a consequence of observing the insulation characteristics of various piston-cylinders under actual working conditions, that the reversal of motion serves better to maintain the piston more nearly in a mean central position within the cylinder. Much carefully planned experimental work is evidently needed to complete our knowledge of this very satisfactory pressure measuring device.

TABLE 3. *Mercury column comparisons made with large pistons.*

| Gage connected to upper end of column | | | | Mercury column | Gage connected to lower end of column | | | Mercury column | |
|---|---|---|---|---|---|---|---|---|---|
| # | $T$ °C | Pressure mm | $T$ °C | Pressure mm | # | $T$ °C | Pressure mm | Total pressure mm | Deviation mm |
| 9 | 29 | 1474.7 | 23.4 | 8137.6 | 8 | 30 | 9611.5 | 9612.3 | −0.8 |
| 8 | 30 | 9611.5 | 23.5 | 8137.5 | 9 | 29 | 17748.2 | 17749.8 | −1.6 |
| 8 | 27 | 9612.1 | 19.7 | 8142.1 | 9 | 26 | 17752.3 | 17755.0 | −2.7 |
| 8 | 28 | 9611.9 | 20.7 | 8140.9 | 9 | 27 | 17752.3 | 17753.6 | −1.3 |
| 9 | 28 | 17751.9 | 20.9 | 8140.7 | 8 | 27 | 25892.0 | 25893.9 | −1.9 |
| 8 | 30 | 25890.3 | 22.7 | 8138.5 | 9 | 29 | 34029.1 | 34039.7 | −1.6 |
| 8 | 30 | 25890.3 | 22.3 | 8139.0 | 9 | 30 | 34030.9 | 34031.2 | −0.3 |
| 9 | 31 | 34030.3 | 26.1 | 8134.6 | 8 | 31 | 42162.7 | 42165.2 | −2.5 |
| 8 | 31 | 42162.7 | 26.5 | 8134.0 | 9 | 31 | 50300.5 | 50299.2 | +1.3 |
| 9 | 31 | 50300.5 | 27.1 | 8133.5 | 8 | 29 | 58428.8 | 58432.7 | −3.9 |
| 8 | 27 | 58431.1 | 25.2 | 8135.7 | 9 | 31 | 66577.5 | 66570.7 | +6.8 |
| 8 | 26 | 58432.3 | 19.5 | 8142.5 | 9 | 26 | 66585.9 | 66578.7 | +7.2 |
| 9 | 30 | 66579.3 | 20.3 | 8141.7 | 8 | 27 | 74711.4 | 74713.6 | −2.2 |
| 8 | 29 | 74708.4 | 20.8 | 8141.1 | 9 | 30 | 82853.8 | 82851.7 | +2.1 |
| 9 | 27 | 50304.6 | 21.6 | 8140.0 | 8 | 27 | 58435.9 | 58443.3 | −7.4 |
| 8 | 29 | 58428.8 | 20.8 | 8141.0 | 9 | 30 | 66575.1 | 66577.2 | −2.1 |
| 9 | 28 | 66577.8 | 21.5 | 8140.2 | 8 | 28 | 74713.8 | 74720.1 | −6.3 |
| 8 | 29 | 74712.3 | 21.6 | 8140.1 | 9 | 29 | 82861.0 | 82858.7 | +2.3 |
| 9 | 30 | 82859.3 | 21.7 | 8140.1 | 8 | 30 | 90994.6 | 90997.1 | −2.5 |
| 8 | 23 | 91016.9 | 20.0 | 8142.2 | 9 | 23 | 99157.8 | 99161.6 | −3.8 |
| 9 | 26 | 99153.9 | 20.7 | 8141.4 | 8 | 25 | 107297.0 | 107299.1 | −2.1 |
| 8 | 29 | 107288.3 | 21.9 | 8140.1 | 9 | 27 | 115428.0 | 115430.5 | −2.5 |
| 9 | 22 | 115439.5 | 22.0 | 8140.0 | 8 | 22 | 123583.9 | 123582.0 | +1.9 |

## SUMMARY

(1) The method of extending comparisons of the piston type pressure gage with a mercury column used by Holborn and Schulze has been

modified. The modifications consist of (1) water jacketing the column to secure constancy of temperature, (2) providing fixed electrical contacts at both ends of the column which with the aid of a sensitive device for injecting or withdrawing mercury provides an invariable column length of mercury, (3) an arrangement of steel stopcocks and water jacketed oil line from the top of the column whereby both gages may be used at the floor level.

(2) Series of comparisons have been made of two pairs of piston gages of different effective areas with a mercury column (875 cm long) in a water-jacketed steel tube to 160 atm. for the larger piston and to 587 atm. for the smaller piston.

(3) The larger piston indicates true pressures to the limit of pressure for which it was designed; 160 atm. The average deviation of the true and indicated pressures is one part in 40,000.

(4) The smaller piston indicates slightly higher pressures than the true pressure beginning at about 400 atm. The deviation increases to one part in 11,000 at 587 atm.

(5) The causes of the discrepancy at the higher range of pressure for the smaller piston cannot be adequately discussed until further investigations have been completed. These investigations are concerned with the precise effects dependent on closeness of fit of the piston in its cylinder, and the changing conditions of oil flow along the piston at higher pressures as well as the distortion of the cylinder due to the mounting and pressure effects on both cylinder and piston.

To interpret length of mercury column as pressure, the compressibility of mercury as a function of the pressure should be accurately verified and also the dependence of temperature expansion on pressure.

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# THE ULTRAVIOLET ABSORPTION SPECTRA AND THE PHOTOCHEMICAL DECOMPOSITION OF GASEOUS HYDROGEN BROMIDE AND IODIDE

by

Harold C. Tingey and Roscoe H. Gerke

[Reprint from the Journal of the American Chemical Society, **48**, 1838 (1926).]

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 180]

# THE ULTRAVIOLET ABSORPTION SPECTRA AND THE PHOTOCHEMICAL DECOMPOSITION OF GASEOUS HYDROGEN BROMIDE AND IODIDE

BY HAROLD C. TINGEY[1] AND ROSCOE H. GERKE

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The purpose of this investigation was to study the ultraviolet absorption spectra of the hydrogen halides during photochemical decomposition in order to test the validity of two alternative mechanisms which have been suggested to explain the existing experimental facts.

Before the quantum theory of band spectra of molecules had received its great development Warburg[2] suggested the following mechanism, which was in accord with his experimental observations. The absorption of a quantum of ultraviolet light decomposed a single hydrogen halide molecule into atoms which late reacted with another hydrogen halide molecule in such a manner as to produce one hydrogen and halogen molecule. More recently Stern and Volmer,[3] in view of the recent developments on the theory of band spectra have assumed that the absorption of the radiation did not produce direct photochemical decomposition, but that it did produce an excited molecule which would, upon collision with another hydrogen halide molecule produce one hydrogen and halogen molecule. With the aid of the quantum theory of band spectra[4] it is possible to predict the type of absorption spectrum which corresponds to either of the above mechanisms. Thus, a band absorption spectrum would be expected to be found if the Stern and Volmer mechanism were correct. On the other hand, if Warburg's mechanism were true the absorption spectrum would not consist of bands, but would probably be continuous, which is analogous to atomic absorption spectra of similar origin.

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[1] From the Doctor's Dissertation of Harold C. Tingey, Massachusetts Institute of Technology.

[2] Warburg, *Sitzb. preuss. Akad. Wiss.*, **1916**, 314; **1918**, 300.

[3] Stern and Volmer, *Z. wiss. Phot.*, **19**, 275 (1920).

[4] Sommerfeld, "Atomic Structure and Spectral Lines," translated from third German Edition by Henry L. Brose. E. P. Dutton and Company, New York, **1923**.

The absorption spectra found for pure hydrogen bromide and hydrogen iodide in this research appear continuous. Reasons are given which support the thesis that they are truly continuous and the results are in agreement with Warburg's mechanism.

## Experimental Part

Hitherto, a monochromatic light source has been the ideal in exact photochemical experimentation. On the contrary, in this research a source of light which emits a continuous spectrum was necessary to reveal the structure of the absorption spectrum. The experimental procedure consisted in photographing the ultraviolet spectrum of a source of light which emitted a continuous spectrum with and without the interposition of a quartz-absorption tube containing the pure gaseous hydrogen halide.

**The Vacuum Line.**—This was constructed of Pyrex glass, and was pumped by a mercury diffusion pump, backed up by an oil pump capable of producing a vacuum of 0.001 mm. The McLeod gage read down to 0.00001 mm., and with the pumps going the pressure could be reduced much further.

**Sources of Ultraviolet Radiation.**—For a reference standard, the cadmium spark spectrum was used. It was excited by high frequency current from a coil for this purpose discharging at about 3000 volts between cadmium electrodes.

For the production of band absorption spectra, a source of continuous ultraviolet radiation is necessary, and it is highly desirable that the intensity should be uniform throughout the range of wave lengths. Good results cannot be obtained with a metal spark spectrum on account of the lines. The source used in these experiments was a hydrogen discharge tube. It was made of 6mm. Pyrex glass tubing, with a polished quartz window 1 mm. thick cemented with de Khotinsky cement on one end. The electrodes were tungsten wire spirals. The tube was filled with dry electrolytic hydrogen at about 15 mm. pressure, the optimum operating pressure being determined by slowly reducing the pressure while the discharge was passing. The current was supplied by the high frequency coil. An intense, striated discharge resulted, blue at first, but changing to pink as the tube became hot.

The radiation from this tube was focused on the spectrograph slit, and the spectrum was continuous and uniform,[5] without lines, for wave lengths between 4000 Å. and 2000 Å., the short-wave limit of the spectrograph used. The spectrum showed lines (unidentified) in the visible and near ultraviolet down to 4000 Å., but these did not interfere with the present experiments. The one draw back to this source was that it required exposures of about an hour, compared with one minute for the cadmium spark.

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[5] The intensity fell off in the region 2200–2000 Å.

**The Spectrograph.**—A small Fery spectrograph, manufactured by Ch. Beaudouin, was used. A cylindro-spherical quartz lens throws an elongated image of the source on the slit. Light from the slit enters the prism, is reflected from its curved back, and is thus focused on the photographic plate. Three exposures could be made on one plate. The entire spectrum from 8000 Å. to 1800 Å. was obtained in one exposure, and covered a length of about 8 cm. The plates used were the Eastman Kodak Company Seed's L. Ortho Plates. They were developed in pyro-tank developer at 17° for 30 minutes.

**The Absorption Tubes.**—Two absorption tubes made entirely of transparent fused quartz were used in the experiments. Both were cylindrical, of 4 cm. diameter. Tube No. 1 was 12 cm. long, and had two side arms, distant about 3 cm. from the ends. Tube No. 2 was 23 cm. long, and had a single side arm near one end. The ends were clear and polished and were about 1 mm. thick. During most of the experiments the side arms were sealed by means of graded seals to Pyrex glass, so that the tubes could be joined directly to the rest of the apparatus without the use of cemented joints. This, together with the all-quartz construction of the tubes, made it possible to evacuate them at high temperatures, thus eliminating absorbed impurities.

Tube No. 3, used in some of the experiments, was a length of Pyrex tubing 90 cm. long and 20 mm. in diameter, with quartz end-windows 1 mm. thick cemented on with de Khotinsky cement.

**Preparation and Purification of the Hydrogen Halides.**—The hydrogen halides were prepared by dropping 85% orthophosphoric acid, of analytical grade of purity, on the potassium salts (prepared by five recrystallizations of the c. p. product), in the apparatus of Fig. 1. A dropping funnel A is fitted by ground-glass joint B into a 250cc. flask C, which contains the salt. D is a trap to condense water, E a phosphorus pentoxide tube containing a vertical column of this substance about 20 cm. long. The system was evacuated to 0.0001 mm., then orthophosphoric acid (previously boiled) was admitted, and the reaction was started by warming. The hydrogen halide, with some water, passed through D, where most of the water condensed; then through E, where the rest of the water was removed; and finally to the trap F, where it was condensed by liquid air. The 4-liter bulb H, evacuated to 0.0001 mm., was shut off at G during this procedure. When enough material had collected in F, the apparatus was sealed off at J, and the system thoroughly evacuated through I, keeping the hydrogen halide frozen. The stopcock I was then closed, and the gas allowed to evaporate through G into H; the last portion, which contained visible amounts of free halogen, was rejected. In this way a bulb of the hydrogen halide at atmospheric pressure, free from water, and from phosphorus and mercury compounds, was obtained. The freshly prepared material froze to a pure white solid; it melted sharply and at constant pressure; this pressure (as read on a capillary manometer) was within 2 mm. of that calculated from the equations of Henglein[6] for the vapor pressures of hydrogen bromide and iodide. Hydrogen bromide, and to a greater extent hydrogen iodide, decomposed slowly on standing in these bulbs, giving free halogen, which also attacked the stopcock grease. Impurities thus introduced were, however, removed in filling the absorption tubes as described below.

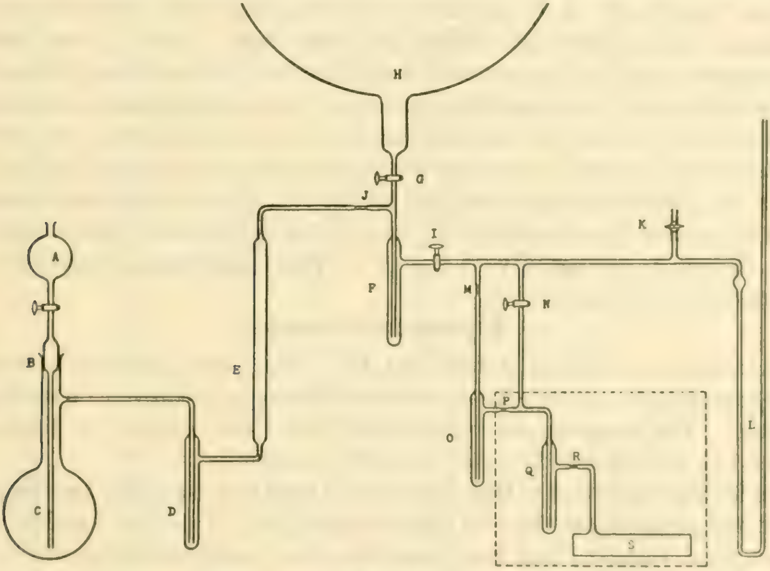

Fig. 1.

**Filling the Absorption Tubes.**—In the first experiments, hydrogen bromide was led directly from the generator into the absorption tube; spectrographic evidence was obtained of an impurity, and thereafter the gas was purified by distillation as follows.

Referring to Fig. 1, F-G-H-I is the storage bulb previously described; stopcock K affords connection to the vacuum line and McLeod gage; L is a mercury manometer on which pressures from 0 to 2 atm. could be read; O and Q are traps; S is the absorption tube. The portion of the apparatus inclosed by the dotted lines can be surrounded by an electrically heated oven.

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[6] Henglein, *Z. Physik*, **18**, 64 (1923).

The system was thoroughly pumped out with the stopcock I open; then the oven was heated to 550°, and the pumping continued for an hour at this temperature. During the heating appreciable amounts of gas, consisting mainly but not entirely of water vapor, were given off. During the last half hour, the stopcock N was closed, and the trap O immersed in liquid air. The oven was removed, and the liquid air transferred to trap Q. In this way it is believed that all water and mercury vapors were removed and kept from the tube S. The trap O was sealed off at H and P before it warmed up. Now with the stopcock I closed, all the gas in H was condensed and frozen in F, and allowed to evaporate back into H until the material had melted and boiled for some time. Then G was closed; the material left in F was frozen, and allowed to sublime slowly from F to Q (which was still surrounded by liquid air), until enough had accumulated. Then with I closed the material in Q was evaporated until the desired pressure was reached, when the absorption tube was sealed off at R.

It was found that the baking out had no effect on the spectrum obtained, so this procedure was omitted in most of the experiments except those on the electrical conductivity of the gas. The redistillation, however, was carried out in all cases.

## Experimental Results

*Absorption of Spectra of HBr and HI.*—The tables give the results of the experiments on the absorption of radiation by hydrogen bromide and iodide. The temperature was that of the room except in Expts. 9, 10 and 11 when it was 25°, 250° and 400°, respectively.

In Tables I and II, the time given is the length of exposure; the temperature and pressure are those of the absorbing gas; "Tube No." refers to the absorption tube; "Plate No." identifies the photographic plate; "L" is the length in centimeters of a column of the gas at one atmosphere pressure, equivalent in absorption to the absorbing gas (assuming Beer's law). It is calculated by the equation, $L$ = Pressure/76. The results are arranged in order of increasing "$L$." The term absorption limit will be made clear below.

The absorption spectra of hydrogen bromide and iodide appeared continuous, showing no evidence of lines or bands. To determine whether our instrument gives high enough resolution to show the separate partial bands of a possible electronic band system, the following calculations were made. The center of the fundamental infra-red band of hydrogen bromide[7] at 3.9$\mu$, is at wave number $v = 2560$, where $v = I/$wave length in cm. Hence the separation of the centers of the partial bands in the ultraviolet band system would be, in wave numbers, approximately $v = 2560$. If $L$

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[7] Imes, *Astrophys. J.*, **50**, 25 (1919).

TABLE I

HYDROGEN BROMIDE

| No. | Time, min. | Press. Cm. of Hg | $L$ | Absorp. limit | Tube No. | Plate No. | Notes |
|---|---|---|---|---|---|---|---|
| 1 | 60 | 0.9 | 0.25 | 2270 Å. | 2 | 28b | 4 |
| 2 | 40 | 4 | 1.2 | 2350 | 2 | 27c | |
| 3 | 30 | 4 | 1.2 | 2340 | 2 | 28a | 4 |
| 4 | 100 | 2 | 2.4 | 2380 | 3 | 30c | |
| 5 | 100 | 7 | 8 | 2430 | 3 | 30b | |
| 6 | 30 | 37 | 11 | 2480 | 2 | 26a | |
| 7 | 65 | 37 | 11 | 2480 | 2 | 26b | |
| 8 | 45 | 76 | 12 | 2460 | 1 | 19a | 1, 2 |
| 9 | 60 | 45 | 13.5 | 2480 | 2 | 38a<br>39a | 5 |
| 10 | 60 | 45 | 13.5 | 2480 | 2 | 38b | 5 |
| 11 | 60 | 45 | 13.5 | 2480 | 2 | 38c<br>39b | 5 |
| 12 | 100 | 14 | 16.5 | 2520 | 3 | 30a | |
| 13 | 100 | 70 | 21 | 2560 | 2 | 35a | 5 |
| 14 | 90 | 76 | 23 | 2570 | 2 | 24a | 1, 3 |
| 15 | 100 | 38 | 45 | 2580 | 3 | 29c | |
| 16 | 50 | 152 | 46 | 2520 | 2 | 21a | 1 |
| 17 | 100 | 152 | 46 | 2520 | 2 | 21c | 1 |
| 18 | 95 | 152 | 46 | 2600 | 2 | 25a | |
| 19 | 40 | 152 | 70 | 2900 | 1 and 2 | 22b | 1 |
| 20 | 100 | 152 | 70 | 2800 | 1 and 2 | 23b | 1 |
| 21 | 100 | 76 | 90 | 2630 | 3 | 29a | |

TABLE II

HYDROGEN IODIDE

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 22 | 100 | 0.2 | 0.25 | 2600 Å. | 3 | 32b | 6 |
| 23 | 100 | 1 | 1.2 | 2960 | 3 | 32a | 6 |
| 24 | 100 | 20 | 24 | 3140 | 3 | 31c | 6 |
| 25 | 100 | 43 | 51 | 3230 | 3 | 31b | 6 |
| 26 | 100 | 120 | 142 | 3300 | 3 | 31a | 6 |

Notes: 1. Gas not purified by distillation; band spectrum present. 2. Gas was moist. 3. Visible amount of $Br_2$ present. 4. Absorption limit poorly defined. 5. Absorption tube baked out at 550°. 6. During experiments on HI, a red substance probably $HgI_2$, formed in tube.

and $L'$ are the wave lengths in centimeters of the centers of two adjacent bands, then $v = (1/L) \times (1/L')$, or $L = L'/(L'V + 1)$. Placing $L' =$ 2500 Å. = 0.000025 cm. (the region in which hydrogen bromide absorbs), the value of $L$ is 2350. That is, the centers of the bands of hydrogen bromide would be separated by 150 Å., or 0.5 cm. on our photographic plates. By a similar calculation it can be shown that the separation of the lines in a partial band would be 1.25 Å. Our instrument would not resolve such lines; but if the lines from two adjacent bands were to merge into a uniform continuous spectrum, each band would have to contain 150/1.25 = 120 lines, of uniform intensity. As this is highly improbable, it appears that hydrogen bromide and iodide have no electronic band absorption spectra.

In the first experiments, a band absorption spectrum was observed extending from 3100 Å. to 2830 Å., approximately, and having 14 flutings in this range. In these experiments the gas was passed over phosphorus pentoxide; the impurity was probably a compound of phosphorus. The fact that this spectrum was eliminated by distilling the gas shows that it was not due to hydrogen bromide. The region of continuous absorption extended from the far ultraviolet (2000 Å.) to a long wave limit, designated as the absorption limit in the table, which depended on the mass of gas traversed by the radiation. This absorption limit was not absolutely sharp, but the transition from apparently complete absorption to apparently complete transmission occurred within a short range of wave lengths (about 30 Å.). The variation of the absorption limit with $L$ can be seen from the tables, and also from the plot in Fig. 2. As the mass of the absorbing gas increases, this limit approaches a limiting value, which is about 2640 Å. for hydrogen bromide and 3320 Å. for hydrogen iodide. These values agree with those found by Coehn and Stuckardt,[8] which were about 2650 Å. for hydrogen bromide and 3340 Å. for hydrogen iodide. Varying the pressure from 0.01 atmosphere to 2 atmospheres has no effect

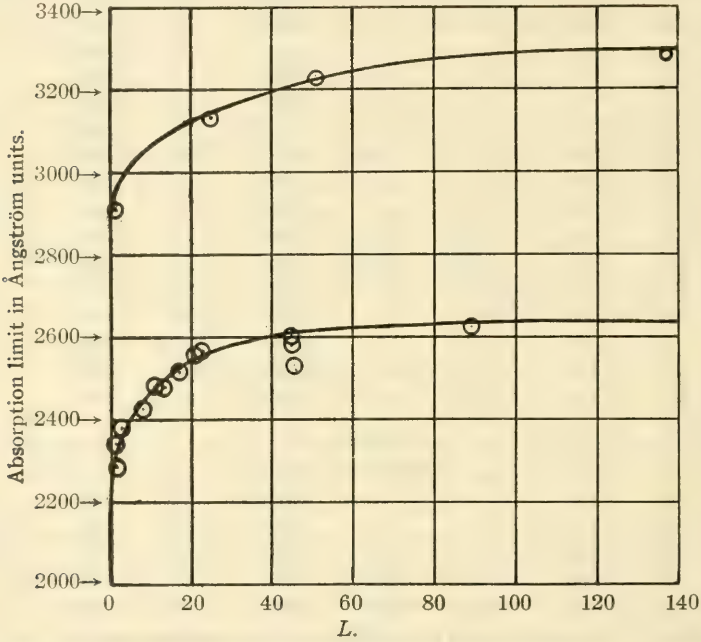

Fig. 2.—Absorption limits and wave lengths.

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[8] Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916).

on the nature of the spectrum; nor does it affect the absorption limit, as long as $L$ remains the same. (Compare Nos. 7 and 8; 15 and 18 in Table II.) Varying the temperature from 25° to 400° does not affect the nature and intensity of the absorption, or the absorption limit (compare Nos. 9, 10 and 11 in Table II). These observations on the effect of temperature and pressure also confirm those of Coehn and Stuckardt.

### Attempts to Excite an Emission Spectrum of Hydrogen Bromide

A tube similar to the hydrogen tube fitted with aluminum electrodes was filled with hydrogen bromide at 1.5 mm. pressure, and current from the coil passed through it. A blue-red discharge resulted; the electrodes were rapidly attacked, and a white substance, probably aluminum bromide, deposited on the inside of the tube. A plate exposed for 30 minutes showed a continous spectrum and lines in the visible identical with the continuous hydrogen spectrum described above. Superposed on this continuous background in the ultraviolet were several lines due to aluminum, and a group of bands between 2880 Å. and 2760 Å. This group consisted of nine bands, arranged in three sub-groups of three each; the spacing in each sub-group and between sub-groups was fairly uniform. These bands occurred outside the limits of absorption for hydrogen bromide; the carrier was not identified, but it is not considered probable that it was hydrogen bromide.

Another attempt was made to excite an emission spectrum of HBr, using active nitrogen. The usefulness of this method has been pointed out by Mulliken.[9] Our apparatus was essentially the same as his. The nitrogen was prepared by heating air in the presence of yellow phosphorus for some time, and passing the resulting gas through concd. sulfuric acid, a phosphorus pentoxide tube, and a liquid-air trap. The liquid-air trap was found necessary to eliminate a brilliant blue spectrum, probably due to phosphorus, which occasionally appeared in the afterglow tube. The spectrum of active nitrogen then appeared in the afterglow tube. On admitting hydrogen bromide to the afterglow tube, the glow disappeared, and a spectrogram showed that the active nitrogen bands had been suppressed completely, or nearly so, in the region of 3300 Å. to 2000 Å., and in the visible region. The only other effects observed on admitting hydrogen bromide were the appearance of a pair of lines at about 3360 Å., and of a system of four bands at about 4000–3650 Å. Since neither of these lies within the limits of absorption for hydrogen bromide, they are not of interest in connection with its absorption spectrum.

### Experiments on the Electrical Conductivity of the Illuminated Gas

As ionization is a possible result of the absorption of radiation, efforts were made to test the electrical conductivity of the illuminated gas. Unfortunately the apparatus available was not sufficiently sensitive to give conclusive results. The conductivity cell consisted of quartz tube No. 1, down one arm of which were inserted parallel tungsten wire electrodes, about 2 mm. apart, sealed through glass which was sealed directly to the quartz with the aid of a graded seal. The tube was filled with hydrogen bromide gas with precautions as to baking out the tube and purifying the gas. Ultraviolet radiation from a cadmium spark source was focused on the region between the two electrodes, and the electrodes were connected to an electroscope. The rate of leak of the charge of the electroscope was observed with and without irradiation. No conductivity was detected; but the high rate of leakage of the cell itself (due to the fact that the electrodes were sealed through the glass only about 0.5 cm. apart) made it doubtful whether currents of the expected order of magnitude could be detected.

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[9] Mulliken (a) *Phys. Rev.*, **25**, 119, (b) 259 (1924); (c) **26**, 1 (1925).

## Discussion

This investigation has shown within the limits of the accuracy of the spectrograph used that the ultraviolet absorption spectra of hydrogen bromide and hydrogen iodide are continuous, showing no evidence of band structure. This result may be discussed from two points of view: first, that of the theory of molecular band spectra; and second, that of the mechanism of the photochemical decomposition.

The type of molecular absorption spectrum which has hitherto received most attention consists of a system of bands, and is ascribed to excitation of a molecule which, in its initial and final states, is the same chemical species. The separation of the individual lines in the partial bands is greatest for those molecules having the smallest moments of inertia. Hence, a heavy molecule with a large moment of inertia gives an absorption spectrum which might appear continuous, if the dispersion of the spectrograph were not sufficiently great. In the case of hydrogen bromide and iodide, the theory of band spectra indicates that the separation of the partial bands (expressed in wave numbers) should be approximately equal to the wave number of the zero line of the fundamental vibrational-rotational absorption band in the infra-red region of the spectrum. In the section on experimental results, it has been shown that our spectrograph is capable of resolving bands of this separation, but no bands were found.

Since the spectra appear to be continuous, it is logical to attempt to correlate them with the continuous absorption spectra shown by atoms. The absorption of light is continuous for the principal line series spectra of atoms if the frequency of the radiation is greater than the series limit, which corresponds to the complete ejection of an electron from the atom.[10] In other words, the atom becomes ionized, and the final state of the reaction is not merely an excited atom, but a positive ion and an electron. X-ray absorption spectra are another example of this phenomenon. In the case of the hydrogen halides, it has been shown by Warburg[2] and others that the absorption of ultraviolet light is accompanied by decomposition into hydrogen and halogen. It is difficult to escape the conclusion that in this case, as in cases of truly continuous absorption, the final state of the absorbing molecule is not the same chemical species as the initial state. Possible final states are (1) hydrogen and halogen atoms, (2) hydrogen halide ion and electron, (3) hydrogen ion and halogen ion. Although sufficient evidence is not at hand to make absolutely sure, it seems most probable that the first of these hypotheses is correct, since in determinations of ionization potentials by electron impact in these gases,[11] no ionization is found until the kinetic energy of the electrons is far greater than the energy of the radiation which produces photochemical decomposition. Our preliminary search for a photo-electric effect in hydrogen bromide gas gave a negative result. Moreover, the energy of the absorbed radiation is greater than that necessary for the decomposition of the gases into atoms. These heats of dissociation for the hydrogen halides are given in Table III, along with the absorption limit and the energy[12] corresponding to this wave length.

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[10] For discussion and references, see article by Harrison, *Phys. Rev.*, **24,** 466 (1924).

TABLE III

COMPARISON OF PHOTOCHEMICAL AND THERMOCHEMICAL ENERGY OF DISSOCIATION OF HYDROGEN HALIDES

| Halide | Absorption limit, Å. | Energy of radiation, cal. | −ΔH (Thermal decompn.), cal. |
|---|---|---|---|
| HCl | 2200 | 130,000 | 99,500 |
| HBr | 2640 | 108,000 | 78,300 |
| HI | 3320 | 86,000 | 68,000 |

It has been pointed out by Stern and Volmer[3] that the absorption of energy sufficient to dissociate the molecule is not always accompanied by dissociation. For example, the iodine molecule has absorption bands and gives resonance band spectra in the ultraviolet at wave lengths much shorter than that corresponding to the heat of dissociation. The molecules of hydrogen bromide and iodide, however, do not appear to have absorption bands[13] of this type in the ultraviolet but appear to have continuous absorption, which may account for the absence of emission bands.

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[11] Compton and Mohler, "Critical Potentials," *Bull. Nat. Research Council*, **9**, No. 48 (1924).

[12] This is given by $Nh\nu$, where $N$ is Avogadro's number, $h$ is Planck's constant, and $\nu$ is the frequency.

[13] Bands of unusual types have been mentioned by Mulliken [*Phys. Rev.*, **25**, 509 (1925)]. The visible absorption bands of iodine gradually merge and "become lost in a region of apparently continuous absorption which probably means that actual dissociation of the molecule is reached or at least closely approached." Also the emission band of calcium hydride, $CaH_2$, shows a peculiarity which might be attributed to the instability of the molecule in higher vibrational or rotational excited initial states. In addition Mulliken observes the non-occurrence of band emission spectra for polar compounds of the sodium chloride or silver chloride type. Very recently Barker and Duffendack [*Phys. Rev.*, **26**, 339 (1925)] have looked for emission bands in hydrogen chloride in the region 6000 to 2000 Å. in low-voltage arcs and found none.

As regards the mechanism of the photochemical decomposition, two hypotheses have been advanced. Stern and Volmer[3] postulate that the absorption of light produced an electronically excited molecule as the first step, and that in the second step a collision between the excited molecule and a normal molecule resulted in the formation of a hydrogen molecule and a halogen molecule. In view of the previous discussion, this mechanism must be ruled out, since it was shown that the existence of an electronically excited hydrogen halide molecule is highly improbable.

STERN AND VOLMER MECHANISM

(1) $HX$ + radiant energy = $HX$ (excited). (2) $HX$ (excited) + $HX$ (normal) = $H_2 + X_2$.

Warburg's mechanism assumes that the ultraviolet light decomposes a molecule of hydrogen halide into atoms, and that the hydrogen atom on collision with a normal molecule produces a hydrogen molecule and an atom of halogen. The two halogen atoms then unite to form a molecule. This mechanism is shown in the first three of the equations below.

WARBURG'S MECHANISM

(1) $HX$ + radiant energy = $H + X$.
(2) $HX + H = H_2 + X$.
(3) $X + X = X_2$.
(4) $HX + X = X_2 + H$.
(5) $H + H = H_2$.

Equations 4 and 5 represent two other possible secondary reactions. Warburg ruled out Equation 4 on the ground that it is accompanied by an increase in free energy, and so could not take place spontaneously; and he pointed out that Equation 5 has a very small probability of occurrence compared with Equation 2, as the concentration of hydrogen atoms is very small. This mechanism explains the fact, brought out by Warburg's experiments, that one quantum of radiant energy decomposes two molecules of hydrogen halide. The data in Table III show that the energy of the light absorbed is sufficient to bring about Reaction 1, and Warburg showed that Reactions 2 and 3 would be spontaneous. It has been pointed out above that the nature of the absorption spectra indicates such a mechanism, at least as regards the primary reaction. Although Warburg put forward his mechanism before the theory of band spectra had received its great development, no facts have been discovered which disagree with it. Nevertheless, the evidence for it is only circumstantial, and definite proof must await the development of methods of detecting small amounts of hydrogen and halogen atoms, whose duration of existence is probably very short.

Two other possible mechanisms suggested themselves, but were found not to be consistent with the experimental results. The first of these assumed the presence in the gases of polymerized molecules, such as are known to exist in hydrogen fluoride. The absorption spectra of such molecules would possibly appear continuous. Absorption by a double molecule could conceivably produce directly a molecule each of hydrogen and halogen, thus accounting in a simple way for the decomposition of two molecules of HX by one quantum of radiation. If this were the case, however, it would be expected that the absorption would be a function of the temperature and the pressure, since increasing the temperature and decreasing the pressure would both tend to bring about the dissociation of the double molecules. No effect of temperature or of pressure on the absorption was observed by Coehn and Stuckardt, by Warburg, or by ourselves. Photographs of the absorption at 25°, 250° and 400°, on the same plate, keeping the length and conditions of exposure the same (Plates No. 38 and 39, Table I, Nos. 9, 10 and 11) showed no appreciable difference in the nature, limit and intensity of the absorption. Coehn and Stuckardt obtained similar results, and Warburg found the absorption coefficient for the wave lengths he used constant with varying pressure. This mechanism was, therefore, dismissed as improbable. The second possibility was that hydrogen halide molecules are adsorbed on the surface of the quartz vessel, and that this adsorbed film is responsible for the absorption of light and the resultant photochemical decomposition. An adsorbed film, however, would be affected by changes of temperature and pressure in much the same way as polymerized molecules. The above remarks in regard to absorption coefficient also rule out this possibility.

Our conclusions regarding the mechanism of the reaction are as follows. The experiments described, with the aid of the quantum theory of spectra, support the postulate that this is a case of dissociation of a molecule into atoms by the direct action of ultraviolet light. The facts that the absorption spectra are apparently continuous, that two molecules of halide are decomposed per quantum of radiation absorbed, and that the energy of the absorbed radiation is sufficient to produce decomposition of the hydrogen halide molecule into neutral atoms, are strong circumstantial evidence in favor of Warburg's original mechanism for the photochemical decomposition of the hydrogen halides.

## Summary

1. Ultraviolet absorption spectra of carefully purified gaseous hydrogen bromide and hydrogen iodide have been photographed at various temperatures and pressures, using a continuous spectrum from a hydrogen discharge tube as a source of radiation.

2. Attempts were made to excite an emission spectrum of hydrogen bromide in the ultraviolet, with an electric discharge through the gas, and with active nitrogen. No emission spectrum which could be attributed to hydrogen bromide was found.

3. An unsuccessful attempt was made to detect photo-electric conductivity in hydrogen bromide gas while illuminated by ultraviolet light.

4. The photographs of the spectra show no band structure,[14] but do exhibit continuous absorption extending from the limit of the quartz region in the ultraviolet to a long-wave limit (absorption limit). This limit has been found to be 2640 Å. for hydrogen bromide and 3320 Å. for hydrogen iodide. The data support the hypothesis that a case of molecular absorption has been found in which the function of the radiation is not to produce a band spectrum, but to produce direct photochemical dissociation of the molecule into atoms.

5. Mechanisms for the photochemical decomposition of the hydrogen halides have been discussed. The mechanism of Warburg is consistent with all the evidence.

CAMBRIDGE A, MASSACHUSETTS

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[14] Since this manuscript has been written, the absorption spectra of hydrogen bromide at different pressures have been photographed with a spectrograph of much greater dispersion. The photographs show no band structure and the spectra appear continuous. These additional data lend still more support to the assumption that the absorption spectra of the hydrogen halides are truly continuous.

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# THE UNIMOLECULARITY OF THE INVERSION PROCESS

by

George Scatchard

[Reprint from the Journal of the American Chemical Society, **48**, 2259 (1926).]

[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 181]

# THE UNIMOLECULARITY OF THE INVERSION PROCESS

By George Scatchard

Received March 20, 1926 Published September 4, 1926

If the rate of a reaction be defined as that fraction of a reactant present in the system which reacts in unit time, this definition may be expressed mathematically as

$$R = \frac{-\mathrm{d}y/y}{\mathrm{d}t} = \frac{-\mathrm{d}\,ln\,y}{\mathrm{d}t} \tag{1}$$

in which $R$ is the rate, $t$ is the time and $y$ is the quantity of the reactant in the system at the time $t$. Since $y$ occurs in a ratio or in a logarithm, it may be expressed in any units—as mass, as moles or, corresponding to the quantity actually measured in most inversion experiments, as $\lambda - \lambda_\infty$, where $\lambda$ is the optical rotation in a tube of any definite length, and the subscript $\infty$ refers to complete inversion. It is somewhat more convenient to work with another quantity, $r$, defined by the equation

$$r = 0.4343\,R = \frac{-\mathrm{d}\log y}{\mathrm{d}t} \tag{2}$$

It is customary, for unimolecular reactions, to assume that the rate as defined above is constant and to integrate Equations 1 or 2 to determine the numerical value of the rate. However, the very accurate measurements of Pennycuick[1] indicate that the rate of inversion of sucrose increases slightly during the course of the reaction. Therefore, the classical integrated expression should not be applied to these measurements, and Equation 2 cannot be integrated unless $r$ be known as a function of $t$.

The rate at any time may be obtained by determining the slope of a smooth curve through the points obtained by plotting $-\log y$ against $t$. The accuracy of this method may be very considerably increased by plotting $-At - \log y$ against $t$, in which case $r$ is $A$ plus the slope of the curve. $A$ is most conveniently chosen as $(-\log y)/t$ for the last measurement. For Pennycuick's measurements in the more dilute solutions the time interval is so large that even this method is less accurate than the precision of the experimental work warrants. In such a case $-At - \log y$ may be plotted against $\sqrt{t}$, and the slope of the curve so obtained divided by $2\sqrt{t}$ added to $A$ to give $r$ [since $\mathrm{d}x/\mathrm{d}t = (\mathrm{d}x/\mathrm{d}\sqrt{t})(\mathrm{d}\sqrt{t}/\mathrm{d}t) = (\mathrm{d}x/\mathrm{d}\sqrt{t})/(2\sqrt{t})$].

TABLE I

CHANGE OF REACTION RATE WITH FRACTION INVERTED

|  | 0.02 *N* HCl[a] | 0.099 *N* HCl | 0.507 *N* HCl | 0.905 *N* HCl |
|---|---|---|---|---|
|  | 40° | 35° | 35° | 35° |
| $k$ = | 0.000605 | 0.001629 | 0.01045 | 0.02301 |
| Fraction inverted | $r/k$ | $r/k$ | $r/k$ | $r/k$ |
| 0.05 | 0.982 | 0.974 | 0.962 | .... |
| .10 | .989 | .978 | .967 | 0.966 |
| .20 | .995 | .984 | .971 | .969 |
| .30 | .998 | .987 | .975 | .972 |
| .40 | 1.000 | .990 | .978 | .973 |
| .50 | 1.000 | .995 | .981 | .974 |
| .60 | 1.000 | .999 | .983 | .976 |
| .70 | 1.000 | 1.000 | .985 | .979 |
| .80 | 1.000 | 1.000 | .986 | .980 |
| .90 | 1.000 | 1.000 | .988 | (0.978) |

[a] In each case the concentration of sucrose is 171 g. per liter.

In Table I are given the rates obtained by applying this method to the measurements of Pennycuick divided by appropriate constants, $k$, for certain fractions of sucrose inverted. With 0.92 *N* acid the rate is constant within 0.1% after the sucrose is 35% inverted; with 0.099 *N* acid a constant value is not reached until 60% is inverted; the rate with 0.507 *N* acid increases continually; and the rate with 0.905 *N* acid passes through a maximum at 80% inversion. This last phenomenon is probably due to a small error in the determination of the rotation at complete inversion caused by side reactions in the presence of the strong acid. The rates in 0.907 *N* acid after 80% inversion are enclosed in parentheses, and are disregarded in the discussion that follows.

Table II contains the same ratios as Table I, but for definite time in-

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[1] Pennycuick, THIS JOURNAL, **48**, 6 (1926).

Table II

Change of Reaction Rate with Time

| Time, minutes | 0.02 *N* HCl $r/k$ | 0.099 *N* HCl $r/k$ | 0.507 *N* HCl $r/k$ | 0.905 *N* HCl $r/k$ | Eq. 3 $r/k$ |
|---|---|---|---|---|---|
| 5 | .... | 0.969 | 0.967 | 0.971 | 0.971 |
| 10 | .... | .973 | .971 | .973 | .973 |
| 20 | 0.974 | .975 | .976 | .976 | .975 |
| 30 | .978 | .978 | .981 | .980 | .978 |
| 40 | .982 | .981 | .983 | (0.978) | .980 |
| 60 | .987 | .984 | .986 | (0.976) | .984 |
| 80 | .989 | .986 | .986 | .... | .987 |
| 100 | .992 | .988 | .988 | | .989 |
| 150 | .994 | .992 | .... | | .993 |
| 200 | .996 | .996 | | | .996 |
| 300 | .999 | 1.000 | | | .998 |
| 400 to end | 1.000 | 1.000 | | | 1.000 |

tervals after the start of the reaction. The last column contains the ratio calculated by the equation

$$r = k(1 - 0.03\,e^{-0.01t}) \qquad (3)$$

The form of Equation 3 and the values of the numerical constants were obtained empirically from the results for the two solutions more dilute in acid, for which the values of $k$ must be the final values of $r$. Then Equation 3 was used to determine $k$ for the two more concentrated solutions. The agreement is very good. The maximum deviation of the measured rates from those calculated is 0.4%, and the average deviation is 0.13%. A comparison of the two tables shows clearly that the rate is a function, not of the fraction inverted, but of the time.

Combining Equations 2 and 3, we may integrate between the time limits 0 and $t$, or between $t_1$ and $t_2$, to obtain

$$\log \frac{y_0}{y} = k[t - 3(1 - e^{-0.01t})] = kt\left[1 - \frac{3}{t}(1 - e^{-0.01t})\right] \qquad (4)$$

$$\log \frac{y_1}{y_2} = k[t_2 - t_1 - 3(e^{-0.01t_1} - e^{-0.01t_2})]$$

$$= k(t_2 - t_1)\left[1 - \frac{3}{t_2 - t_1}(e^{-0.01t_1} - e^{-0.01t_2})\right] \qquad (5)$$

These expressions divided by $t$ or by $(t_2 - t_1)$ correspond to the classical "specific reaction rate" or "velocity constant." Equation 4 may be compared with the experimental measurements independently of the graphic determination of the slopes. The mean deviations of the average "constants" from those computed by Equation 4 are for the four series: 0.5, 0.3, 1.2 and 0.8%, but the deviations for very short time intervals indicate a constant time error. If the average values be corrected by subtracting from the times the quantities: 0.2, 0.0, 0.1, 0.05 minutes, the mean deviations become: 0.3, 0.3, 0.4, 0.4%, without any trend with time. For the first two series the mean deviation of the individual measurements from their averages is 0.2 and 0.5%, so the agreement with the theory is as good as could be expected, and the time correction does not attribute an unreasonable error to the determination of the time of a reaction started by pouring one solution into another and stopped by pouring through a cooling coil.

From the nature of the change in rate it is possible to draw several conclusions as to the cause of the change. In the graphical method the start of the reaction is treated as any other point on the curve, and any error in the initial rotation or in the time of starting the reaction is completely eliminated after the first few measurements. For the same reason a constant time error, due to the reaction continuing a little during the cooling, would also be without effect. The time error indicated by the integrated Equation 4 is discussed above. There can be no significant error in the final rotation, except for the values enclosed in parentheses, for such an error would give a more rapid change toward the end of the reaction. Lack of thermal equilibrium because of heat produced or absorbed during the reaction would give a larger effect for the more rapid reactions and is therefore excluded.

The increase in rate cannot be caused by a change in the environment as the concentration of sucrose decreases and that of inert sugar increases, for such a change would persist throughout the reaction and would be nearly independent of the acid concentration. Table I shows clearly that the change in reaction rate fulfils neither of these criteria.

Equation 3 may be explained by the attainment of equilibrium in a process originally somewhat displaced from equilibrium for which the rate of attaining equilibrium is proportional to the displacement. This is more clearly shown in the differential form

$$\mathrm{d}r/\mathrm{d}t = 0.01\ (k - r) \qquad (6)$$

Two causes for such a change suggest themselves. The temperature of the solution might be lower than that of the thermostat at the start of the reaction. This explanation would demand that the temperature be 0.2–0.3° too low after 40 minutes in the thermostat, and that five hours be required to attain thermal equilibrium. It is, therefore, highly improbable. The mixing of the solutions might not be quite complete at the start, and true homogeneity might be attained only by diffusion. Five hours does not appear too long for this process, and it seems very probable that pouring the solutions from one flask to another does not result in absolutely complete mixing. It may be concluded that Equations 3 to 6 are characteristic of the technique of Pennycuick but not of the inversion process, and that the rates of inversion do not change more than a few tenths of a per cent. during the course of the reaction. The most probable values of the rates are the *k*'s given in Table I, even for the cases where the measured rates never attain these values.

In the paper of Pennycuick the results are expressed by the classical "reaction velocity," which may be shown from Equations 3 and 4 to change more uniformly than the rate, and the conclusion is reached that the change is due to increasing activity coefficients of the hydrogen ion and of the sucrose. It has been shown above that the present more precise treatment makes these conclusions untenable. The evidence for the increase in the hydrogen-ion activity appears sound, but these results indicate that there must be some compensating tendency to diminish the rate. It is much less certain that the activity coefficient of the sucrose increases during the inversion. The point of view of Pennycuick's paper is very similar to that presented by Moran and Lewis[2] except that other factors considered in the earlier paper are not discussed in the more recent one. This point of view has been criticized in detail in earlier papers.[3]

## Summary

The precise measurements by Pennycuick of the rate of inversion of sucrose have been treated by a mathematical method more accurate than any hitherto applied to reaction rates. The rates have been determined graphically and an equation has been derived relating the change of rate to the time of reaction. From the nature of the change in rate it is shown that several possible experimental errors give no disturbance, and that the change cannot be due to a change in the environment but is most probably due to slightly inefficient mixing. It is concluded that in homogeneous solutions the rates of inversion are constants within a few parts per thousand, and the most probable values of these rates are given.

Cambridge, Massachusetts

[2] Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922).

[3] Scatchard, This Journal, **43**, 2387, 2406 (1921); **45**, 1580 (1923).

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# PUBLICATIONS

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# THE IONIZATION OF WEAK ELECTROLYTES

by

D. A. MacInnes

[Reprint from the Journal of the American Chemical Society, **48**, 2068 (1926).]

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 182]

# THE IONIZATION OF WEAK ELECTROLYTES

BY D. A. MACINNES

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Arrhenius' theory that the degree of ionization can be obtained from the conductance ratio, $\Lambda/\Lambda_0$, is now quite generally conceded to be untrue for strong electrolytes, since it involves the assumption that the mobilities of the ions do not change from infinite dilution to the concentration in question. The properties of a large group of strong electrolytes can, in fact, be most readily explained by the theory that they are completely ionized. The decrease in the value of the equivalent conductance with concentration is, almost certainly, due to decrease in the ionic mobilities, caused by an inter-ionic attraction which steadily gains strength as the concentration increases. If, therefore, Arrhenius' method for computing the degree of dissociation is not valid for strong electrolytes, it seems improbable that it can be used without modification for weak electrolytes since, as will be shown below, the ion concentrations can attain values large enough to cause appreciable changes in the mobilities of the ions.

It has appeared to me, however, that a more nearly correct degree of dissociation can be obtained by comparing the measured equivalent conductance with that of an equivalent of the ions *at the same ion concentration*, a quantity which will be represented by $\Lambda_e$. Thus the degree of dissociation of acetic acid at 0.01 $N$ may be computed by dividing the $\Lambda$ value for that concentration by the equivalent conductance of completely dissociated acetic acid at the ion concentration existing in the 0.01 $N$ solution. Now if solutions of hydrogen chloride, sodium chloride and sodium acetate are all completely dissociated, $\Lambda_e$ for acetic acid can be computed by the simple relation $\Lambda_{e\text{HAc}} = \Lambda_{\text{HCl}} - \Lambda_{\text{NaCl}} + \Lambda_{\text{NaAc}}$, the $\Lambda$ values all being interpolated for the ion concentration of the solution under consideration. This involves a short series of approximations since the value of $\Lambda_e$ for the solution must be known before the value of the ion concentration, $C{\cdot}\Lambda/\Lambda_e$, can be obtained. Plots of $\Lambda$ as ordinates against $C^{1/2}$ as abscissas were found useful for this interpolation as they give nearly straight lines.

If degrees of dissociation, $\alpha$, calculated from the relation $\Lambda/\Lambda_e$ are substituted in the familiar Ostwald dilution law, $K' = \alpha^2C/(1-\alpha)$, the values of $K'$ are found to increase with the concentration. This is shown in Col. 5 of Table I, which is based on Kendall's[1] excellent conductance work. However, it must be recalled that although the product $C{\cdot}\Lambda/\Lambda_e$ gives the correct concentrations of the ions, and $(1-\Lambda/\Lambda_e)C$ that of the undissociated portion, each of these must be multiplied by the appropriate activity coefficient if the law of mass action is to hold. The modified Ostwald dilution law thus becomes,[2] for the acid HA

$$K = \frac{\alpha\gamma_{\text{H}^+}\cdot\alpha\gamma_{\text{A}^-}\cdot C}{(1-\alpha)\ \gamma_{\text{HA}}}.$$

For the undissociated portion the activity coefficient, $\gamma_{\text{HA}}$, has been assumed to be unity, except as mentioned below, since this portion of the solute carries no charge and is otherwise similar to substances that are nearly perfect solutes in aqueous solution, at least at moderate concentrations. The activity coefficients of the ions $\gamma_{\text{H}^+}$ and $\gamma_{\text{A}^-}$ would be expected to change with ion concentration in very nearly the same manner that the activity coefficients of hydrochloric acid solutions vary with the *total* concentration, since the latter substance is completely dissociated. The mean activity coefficients $\gamma$ have been computed from the Debye-Hückel limiting equation $-\log\gamma = 0.5\sqrt{C}$ with the exception of values at the higher ion concentrations which were interpolated from the values given by Scatchard.[3] The last column of the table gives values of the expression: $K = \alpha^2\gamma^2C/(1-\alpha)$. With the possible exception of the figures for acetic acid, the value of $K$ is substantially the same throughout the range of concentrations, being more nearly constant in the more concentrated solutions of the stronger acids where the "ionization constant" computed on the Arrhenius assumptions changes rapidly with the concentration. The agreement of the theory with the computations is the more striking because in each case an error in any one of four series of conductance measurements will affect the value of the constant. Furthermore the constant $K$ is the only empirical constant obtained from the data. Kendall's[4] computations involve two empirical constants, namely, the value of $\Lambda_0$ and the "ionization constant," and even so, the equation based on Arrhenius' assumption fails to fit the data for the stronger acids and the higher concentrations. In my computations the data for the lowest concentrations of

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[1] Kendall, *J. Chem. Soc.*, **101**, 1275 (1912).

[2] After the computations for this paper were completed I learned that Sherrill and Noyes had independently arrived at this equation, in a paper at that time unpublished.

[3] Scatchard, THIS JOURNAL, **47**, 641 (1925).

TABLE I

| Concn. | $\Lambda$ | $\Lambda_e$ | "Ionization constant" $\times 10^4$ | $K'$ $\times 10^4$ | $K$ $\times 10^4$ |
|---|---|---|---|---|---|
| | | | ACETIC ACID | | |
| 0.07369 | 6.086 | 385.7 | 0.1845 | 0.1868 | *0.1743* |
| .03685 | 8.591 | 386.5 | .1851 | .1862 | *.1755* |
| .01842 | 12.09 | 386.9 | .1849 | .1857 | *.1765* |
| .009211 | 16.98 | 388.1 | .1849 | .1844 | *.1769* |
| .004606 | 23.81 | 388.9 | .1851 | .1840 | *.1775* |
| .002303 | 33.22 | 389.2 | .1849 | .1838 | *.1784* |
| | | | *o*-CHLOROBENZOIC ACID | | |
| 0.006662 | 134.6 | 375.8 | 12.93 | 13.31 | *12.03* |
| .003331 | 174.0 | 377.5 | 12.86 | 13.16 | *12.11* |
| .001666 | 218.0 | 378.9 | 12.84 | 13.04 | *12.23* |
| .0008327 | 262.6 | 380.3 | 12.84 | 12.86 | *12.22* |
| .0004163 | 302.1 | 381.1 | 12.79 | 12.54 | *12.16* |
| | | | 3,5-DINITROBENZOIC ACID | | |
| 0.003929 | 175.7 | 373.2 | 16.14 | 16.45 | *15.03* |
| .001860 | 219.0 | 374.9 | 15.99 | 16.12 | *15.08* |
| .0009822 | 262.7 | 376.1 | 15.94 | 15.90 | *15.04* |
| .0004922 | 301.5 | 377.1 | 15.99 | 15.69 | *15.05* |
| | | | CYANO-ACETIC ACID | | |
| 0.05946 | 88.0 | 372.7 | 40.0 | 43.39 | *34.9* |
| .02972 | 117.0 | 375.3 | 39.2 | 42.64 | *34.9* |
| .01487 | 152.5 | 377.9 | 38.3 | 40.61 | *34.9* |
| .007435 | 193.9 | 380.0 | 37.8 | 39.53 | *34.9* |
| .003716 | 238.7 | 382.0 | 37.2 | 38.68 | *35.0* |
| .001858 | 282.6 | 384.0 | 37.2 | 38.12 | *35.2* |
| .0009290 | 320.0 | 385.4 | 37.3 | 37.62 | *35.6* |
| .0004645 | 347.1 | 387.0 | 37.3 | 36.25 | *34.7* |
| | | | *o*-NITROBENZOIC ACID | | |
| 0.03125 | 139.7 | 367.0 | 67.2 | 73.11 | *59.7* |
| .01562 | 179.0 | 369.8 | 66.0 | 70.99 | *60.0* |
| .007812 | 221.9 | 372.3 | 64.5 | 68.70 | *60.0* |
| .003906 | 265.0 | 374.6 | 63.3 | 66.81 | *59.9* |
| .001953 | 303.6 | 376.2 | 62.8 | 65.91 | *60.5* |
| .0009765 | 333.5 | 378.7 | 62.7 | 63.45 | *59.6* |

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[4] The values in the columns headed "ionization constant" are from Kendall's paper.

the acids were not used since it would have been necessary to extrapolate the corresponding conductance data for the sodium salts. I have not found other data than those given of sufficient accuracy to test the questions involved in this paper. It seems fitting to express appreciation of the recent, very accurate measurements of the conductance of dilute solutions of hydrochloric acid by Parker,[5] without which these computations would not have been possible.

The only case in which there is a definite trend in the value of the constant $K$ is that of acetic acid in which there is a change of 2.2% from 0.07 to 0.002 $N$. This is probably due to the fact that the conductance data for the acid and its sodium salt were obtained by different workers.[6] In all the other cases cited Kendall measured both types of data. The trend of the constant for acetic acid is not due to a variation from unity of the activity coefficient $\gamma_{HA}$, of the undissociated acid. Using the method and data given by Lewis and Randall[7] for computing this factor from the freezing points of the more concentrated aqueous solutions of the acid it was found that this activity coefficient at 0.07 $N$ is 0.996 and is progressively nearer unity for lower concentrations. This small correction has been applied to values of $K$ in Table I. A similar computation of the values of this coefficient for the other acids should, of course, be made but the freezing-point data are not at present available. In any case it probably differs very slightly from unity. Another factor, called to my attention by Professor George Scatchard, which is sufficient to cause deviations of the magnitude observed, and which must certainly be considered in a complete theory for these solutions, is an effect on the activities of the ions produced by the change of the dielectric constant with the concentration. This change is not known for conducting solutions, but computations based on the Debye-Hückel theory indicate that for substances similar in composition to acetic acid a variation in $K$ of the magnitude and sign of that observed may be expected. Similar effects might be present for the other acids, but the computations given above do not indicate their presence.

## Summary

Computations, based mainly on Kendall's measurements, show that the mass law holds for a series of organic acids of various strengths, throughout the complete range of concentrations on which conductance measurements have been made, provided (a) that the degrees of ionization are computed in a manner which allows for inter-ionic attraction, and (b) that the resulting ion concentrations are multiplied by the appropriate activity coefficients. The agreement hitherto found with Ostwald's dilution law, for weak electrolytes and for the lower concentrations of "transition" electrolytes, has been found to be due to a compensation of two effects. Arrhenius' method for computing degrees of dissociation yields too low values, and the activity coefficients have been tacitly assumed to be unity, whereas at all low concentrations such coefficients are less than one.

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[5] Parker, This Journal, **45**, 2027 (1923).

[6] The published values for the conductance of sodium acetate show a wide divergence. I have used the data of Lorenz and Osswald, *Z. anorg. Chem.*, **114**, 209 (1920).

[7] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, pp 284-290.

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# SIX PLACE TABLES OF THE DEBYE ENERGY AND SPECIFIC HEAT FUNCTIONS

by

James A. Beattie

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# SIX PLACE TABLES OF THE DEBYE ENERGY AND SPECIFIC HEAT FUNCTIONS

By James A. Beattie

The computation of the following tables was begun in 1920. The Debye[1] equations for energy contents and specific heats of solids had not at that time been completely tested. The only tables of the Debye functions are those contained in Nernst's "Theoretischen und Experimentellen Grundlagen des Neuen Wärmesatzes" (1918) which includes a table for $C_v$ to three significant places calculated for steps of 0.1 in the argument, and a table for $\frac{E}{T}$ to four or three places for steps of 0.01 from 0 to 2, and increments of 0.1 from 2 to 16 in the argument.

As a preliminary to a comparison of the Debye equation with the experimental data, it was decided to compute tables of these functions, having an accuracy of six significant figures. The time has not been available for a study of the experimental data, and hence the tables are now published alone. Since the beginning of the present computations, comparisons of the Debye equations with the data have made it appear improbable that the Debye theory gives a complete explanation of the specific heat of solids. However it is believed that such functions as are here computed will appear in more complete explanations of the specific heat of solids; moreover the same definite integral which occurs in the Debye equation has appeared in other theoretical investigations, and so it has been thought best to present the tables at this time.

The Debye equations are

$$U = \frac{9RT}{x^3}\int_0^x \frac{v^3dv}{e^v-1} \tag{1}$$

$$C_v = 3R\left(\frac{12}{x^3}\int_0^x \frac{v^3dv}{e^v-1} - \frac{3x}{e^x-1}\right) \tag{2}$$

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[1] Debye, Ann. Phys. (IV) 39, 789 (1912).

in which $U$ and $C_v$ are the energy and specific heat at constant volume of a solid, $R$ is the gas constant per *mol*, $T$, the absolute temperature, and $x = \frac{\theta}{T}$, where $\theta$ is a temperature characteristic for each solid, and has the value $\theta = \frac{h\nu_m}{k}$. In this expression $h$ is Planck's constant, $\nu_m$ a frequency characteristic of the substance, and $k$ the value of $R$ divided by the Avagadro number.

Since $R$ is an experimentally determined constant, whose value is known to only about 0.03 per cent, a table should be independent of its absolute value. This end may be conveniently accomplished by noticing that when $T = \infty$, $x = 0$, hence

$$C_{v\infty} = 3R$$ [2]

and we may therefore write

$$\frac{U}{TC_{v\infty}} = \frac{3}{x^3}\int_0^x \frac{y^3dy}{e^y - 1} \tag{3}$$

$$\frac{C_v}{C_{v\infty}} = \frac{12}{x^3}\int_0^x \frac{y^3dy}{e^y - 1} - \frac{3x}{e^x - 1} \tag{4}$$

The functions represented by equations (3) and (4) are the ones presented in Tables I and II.

The definite integral

$$\int_0^x \frac{y^3dy}{e^y - 1} \tag{5}$$

occurs in both equations and is obviously a function of $x$ alone. It can be transformed into the following form[3]

$$\int_0^x \frac{y^3dy}{e^y - 1} = \frac{\pi^4}{15} - x^4 \sum_1^\infty {}_n e^{-nx}\left(\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right). \tag{6}$$

To calculate the value of the integral for each entry in the table from Equation 6 would be very laborious. Hence this equation was used to calculate the function only for each increment of

[2] Debye, loc. cit. pp. 797 and 789.
[3] Debye, loc. cit. pp. 801 and 802.

0.5 in $x$ beginning with the value 1 and ending with 24, sufficient places being carried to give an accuracy of one unit in the tenth significant figure.

The next step was to draw up a table for increments of 0.05 in the argument. For this interpolation, use was made of Simpson's rule in the form

$$\int_a^b f(x)dx = \frac{\Delta x}{3}\left\{ [f(a)+4f(x_1)+f(x_2)]+[f(x_2)+4f(x_3)+f(x_4)] \right.$$
$$\left. \ldots +[f(x_{2n-2})+4f(x_{2n-1})+f(b)] \right\}$$

The value of the integrand $\frac{y^3}{e^y-1}$ was computed for each increase of .025 in $x$, from 1 to 24, *i.e.*, $\Delta x = 0.025$. The application of Simpson's rule gave values of the integral (5) for each increase of 0.05 in the argument. For these calculations the values of $e^y$ were obtained by computing the value of $y \log_{10} e$ and determining the antilogarithms using Vega's Ten Place Tables (Thesaurus Logarithmorum 1794). $y^3$ was obtained from Barlow's Tables. All multiplication and division were carried out with the aid of a mechanical calculating machine. Simpson's rule requires the addition of four quantities for each successive value and hence to pass from 1.0 to 1.5 by steps of .05 requires forty additions. Therefore the number of significant figures retained in $\frac{y^3}{e^y-1}$ were such as to give 12 significant figures in the final value of the integral although only ten were good since the starting value for 1.0 had only 10 significant figures. By this method however no calculation errors were introduced by the use of Simpson's rule. At each successive value of 0.5 in the argument the value of $\int_0^x \frac{y^3 dy}{e^y-1}$ calculated to ten correct figures by Equation 6 was used as a starting point for the next Simpson rule series.

It is interesting to note that Simpson's rule allows of a most accurate calculation of this integral. At the end of each increment of 0.5 in the argument the value of the integral calculated from Simpson's rule was compared with the value calculated by Equation 6. The discrepancies were

| *Series* | *Error by use of Simpson's rule* |
|---|---|
| 1.0−1.5 | 14 in tenth significant figure |
| 1.5−2.0 | 10 in tenth significant figure |
| 2.0−2.5 and successive series | 0 in tenth significant figure |

The function $\frac{y^3}{e^y-1}$ passes through a maximum at about 2.80 and in the range 1.0 to 2.0 differs from a quadratic sufficiently to cause the errors given above. In the first two series the errors were distributed among the results by linear interpolation and these corrected values used for the further computation. The value of the integral was then known to ten significant figures for each increment of 0.05 in $x$ from the value 1 to the value 24, with an allowable error of 2 in the tenth place.

For the next interpolation to increments of 0.01 in the argument, use was made of the trapezoidal rule; since, with this rule, it is possible to obtain a value for the integral for each calculated value of the integrand.

$$\int_a^b f(x)dx = \frac{\Delta x}{2}\left\{[f(a)+f(x_1)]+[f(x_1)+f(x_2)]+\ .\ .\ .\ [f(x_{n-1})+f(b)]\right\}$$

The value of $\Delta x$ was 0.01.

It will be noticed that between any two successive known values of the integral only four unknown values remained, *i.e.*, of the series 1.00, 1.01, 1.02, 1.03, 1.04, 1.05, etc., the value of the integral for the two end figures were known. It was therefore believed that the trapezoidal formula would give results accurate to about 8 places since the range of the interpolation was so small and the spacings of $x$ so close together. The value of $\frac{y^3}{e^y-1}$ was calculated for every increment of .01 in the argument except those values ending in 00 or 05, which had been already determined. Sufficient places were used to give an accuracy of 9 places in the added values of the integral. After each increment of .05 in the argument the value of the integral determined to 10 significant figures by use of Simpson's rule was used for the next series of four values, and also used to check the preceding series.

It was found that for the values of the argument 1.0 to 2.0 it was still necessary to use Simpson's rule in order to obtain the required accuracy. Above 2.0 however the trapezoidal rule gave the required accuracy and was used. From 2 to 3 the maximum error due to the use of this rule for any series of five successive values was 24 in the ninth place, and this was distributed linearly between the four intervening values. Between three and four the maximum discrepancy was 14 in the ninth; from four to five, 4 in the ninth; and above five, two in the ninth place.

The value of the integral $\int_0^x \frac{y^3dy}{e^y-1}$ was now known for each .01 increase in $x$ from 1 to 24, with an accuracy of ten places for those values ending in 0 or 5 and to nine places for those ending in 1, 2, 3, 4, 6, 7, 8, or 9.

The functions of Equations (3) and (4) were then computed, using in every case nine significant figures (all the figures in $x^3$ were used) until the last operation had been finished when the resulting values were rounded off to eight places. The first and second differences were determined and the values so adjusted that the second differences were smooth.

For the interval 0 to 1 in the argument $\frac{C_v}{C_{v\infty}}$ was expanded into a power series in $x$,[4] giving the result

$$\frac{C_v}{C_{v\infty}} = \frac{12}{x^3}\int_0^x \frac{y^3dy}{e^y-1} - \frac{3x}{e^x-1}$$

$$= 1.0 - 0.05x^2 + 1.78571429\times 10^{-3}x^4 - 5.511464\times 10^{-5}x^6$$

$$+ 1.57828\times 10^{-6}x^8 - 4.336\times 10^{-8}x^{10} + 1.16\times 10^{-9}x^{12} - 3\times 10^{-11}x^{14}.$$

The value of this sum was computed to ten significant figures for each increment of .01 in $x$. In order to obtain $\frac{U}{TC_{v\infty}}$, it is necessary to add $\frac{3x}{e^x-1}$ (which must be known to ten significant figures) and divide by four. It is therefore necessary to know the value of $e^x$ to twelve places for the smaller values of $x$, since two places are lost when 1 is subtracted. In order to obtain this accuracy we notice that

---

[4] Debye, loc. cit. p. 799.

$$\begin{aligned} e^{x+h} &= e^x e^h \\ &= e^x\left(1+h+\frac{h^2}{2!}+\frac{h^3}{3!}+\frac{h^4}{4!}+\frac{h^5}{5!}+\ldots\right) \end{aligned}$$

and when $h=.01$

$$e^{x+.01}=1.010050167084168\ e^x$$

and hence beginning with $e^0=1$ it is possible to obtain $e^x$ for each step of .01 in $x$ from 0 to 1 by multiplication. The values of $\frac{U}{TC_{v\infty}}$ and $\frac{C_v}{C_{v\infty}}$ so computed were rounded off to eight significant places, and the first and second differences made and smoothed.

A new six place table was then typewritten from the eight place table, all values ending in 50 or over in the eighth place being increased one unit in the sixth. The six place table was differenced for first and second differences and the second differences studied for smoothness in all cases where, in the eight place table, the last two figures were between 47 and 53. In the final six place table two successive differences never differ by more than two units in the last place; *i.e.*, a run of 8, 8, 9, 7, 8, 8, may occur but not 8, 8, 9, 6, 8, 8. It is believed that the maximum error in the final table is one unit in the sixth significant figure and that this should not occur very often.

The table ends for the argument 24, since, above this value, the functions can be calculated to six significant places from a simple cubic expression. From Equation 6 when $x=24$, we have

$$\int_0^{24}\frac{y^3}{e^y-1}\,dy=\frac{\pi^4}{15}-0.00000059$$

$$=6.49393940-0.00000059$$

and since $\int_0^{\infty}\frac{y^3}{e^y-1}\,dy=\frac{\pi^4}{15}$

the error introduced by neglecting the area under the curve from $x=24$ to $x=\infty$ is six in the eighth significant figure. The value of

$\frac{3x}{e^x-1}$ for $x=24$ is .0000000027 and this term can also be neglected since it does not affect the sixth significant figure of $\frac{C_v}{C_{v_\infty}}$ which has the value 0.00563710 when the argument is 24. For greater values of $x$ the errors introduced by these simplifications are still smaller. Hence we can set

$$\frac{U}{TC_{v_\infty}}=\frac{\pi^4}{15}\times\frac{3}{x^3}$$

$$=\frac{19.481818}{x^3} \qquad \text{when } x>24$$

$$\frac{C_v}{C_{v_\infty}}=\frac{\pi^4}{15}\times\frac{12}{x^3}$$

$$=\frac{77.92727}{x^3} \qquad \text{when } x>24$$

The tables are given in the succeeding pages. It is suggested that for $3R$, *i.e.*, $C_{v_\infty}$, the value 5.9613 be taken if the 15° calorie is used in the measurement of energy, 5.9665 if the 20° calorie is used, and 24.9431 if the joule is used.

In order to obtain $\theta$ the characteristic temperature from data on specific heat, it is necessary to divide $C_v$ for the temperature $T$ by 5.9613 ($C_{v_\infty}$) and determine the argument $x$ corresponding to the measured value of $C_v$ from Table II. Multiplication of $x$ by $T$ gives $\theta$. To obtain the total energy at any temperature $T$ knowing $\theta$, it is necessary to determine $x$ by dividing $\theta$ by $T$, and find the value $\frac{U}{TC_{v_\infty}}$ corresponding to the known value of $x$ from Table I. The value of $U$ at the temperature $T$ is then found by multiplying this value by $T$ and by 5.9613. For values of $x>24$ use the equations given at the bottom of the tables.

## Summary

Tables to six significant figures of the Debye energy and specific heat functions

$$\frac{U}{3RT}=\frac{3}{x^3}\int_0^x\frac{y^3dy}{e^y-1}$$

$$\frac{C_v}{3R}=\frac{12}{x^3}\int_0^x\frac{y^3dy}{e^y-1}-\frac{3x}{e^x-1}$$

have been prepared for values of $x$ from 0 to 24. The variable $x$ has the value $\frac{\theta}{T}$ where $\theta$ is a "characteristic temperature" of the solid in question and $T$ is the absolute temperature at which $C_v$ and $U$ are measured. For $3R$ the value 5.9613 calories per degree is suggested when the energy is measured in terms of the 15° calorie and 24.9431 if the joule is used. It is believed that the maximum error in the tables is one unit in the sixth significant place.

For values of $x$ greater than 24 an error of less than one in the sixth significant figure is introduced by using the simple equations

$$\frac{U}{3\,RT}=\frac{19.481818}{x^3}$$

$$\frac{C_v}{3R}=\frac{77.92727}{x^3}$$

Cambridge, Mass.

# TABLE I

## DEBYE ENERGY FUNCTION

$$\frac{U}{3RT} = \frac{3}{x^3}\int_0^x \frac{y^3dy}{e^y-1}$$

|  |  |  |  |  | $U/3RT$ |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0.0 | 1.000000 | 0.996255 | 0.992520 | 0.988795 | 0.985080 | 0.981375 | 0.977680 | 0.973995 | 0.970320 | 0.966655 |
| 0.1 | .963000 | .959355 | .955720 | .952095 | .948480 | .944875 | .941280 | .937695 | .934119 | .930554 |
| 0.2 | .926999 | .923454 | .919919 | .916393 | .912878 | .909373 | .905877 | .902392 | .898916 | .895451 |
| 0.3 | .891995 | .888550 | .885114 | .881688 | .878272 | .874866 | .871470 | .868084 | .864708 | .861341 |
| 0.4 | .857985 | .854638 | .851302 | .847975 | .844658 | .841351 | .838053 | .834766 | .831489 | .828221 |
| 0.5 | .824963 | .821715 | .818477 | .815248 | .812030 | .808821 | .805622 | .802433 | .799253 | .796083 |
| 0.6 | .792923 | .789773 | .786633 | .783502 | .780381 | .777270 | .774168 | .771076 | .767994 | .764921 |
| 0.7 | .761858 | .758805 | .755762 | .752728 | .749703 | .746689 | .743684 | .740688 | .737702 | .734726 |
| 0.8 | .731759 | .728802 | .725854 | .722916 | .719987 | .717068 | .714159 | .711259 | .708368 | .705487 |
| 0.9 | .702615 | .699753 | .696900 | .694057 | .691223 | .688398 | .685583 | .682777 | .679981 | .677193 |
| 1.0 | .674415 | .671647 | .668888 | .666138 | .663397 | .660666 | .657944 | .655231 | .652527 | .649833 |
| 1.1 | .647148 | .644472 | .641805 | .639147 | .636498 | .633859 | .631228 | .628607 | .625995 | .623392 |
| 1.2 | .620798 | .618213 | .615637 | .613070 | .610512 | .607963 | .605422 | .602891 | .600369 | .597856 |
| 1.3 | .595351 | .592856 | .590369 | .587891 | .585422 | .582962 | .580511 | .578068 | .575634 | .573209 |
| 1.4 | .570793 | .568386 | .565987 | .563596 | .561215 | .558842 | .556478 | .554122 | .551775 | .549437 |
| 1.5 | .547107 | .544785 | .542472 | .540168 | .537872 | .535585 | .533306 | .531036 | .528774 | .526520 |
| 1.6 | .524275 | .522038 | .519809 | .517589 | .515377 | .513174 | .510979 | .508792 | .506613 | .504442 |
| 1.7 | .502280 | .500126 | .497980 | .495842 | .493712 | .491590 | .489477 | .487371 | .485274 | .483184 |
| 1.8 | .481103 | .479030 | .476964 | .474907 | .472857 | .470816 | .468782 | .466756 | .464738 | .462728 |
| 1.9 | .460726 | .458731 | .456745 | .454766 | .452794 | .450831 | .448875 | .446927 | .444987 | .443054 |

*U*/3*RT*

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 2.0 | 0.441128 | 0.439211 | 0.437301 | 0.435398 | 0.433503 | 0.431616 | 0.429736 | 0.427864 | 0.425999 | 0.424141 |
| 2.1 | .422291 | .420448 | .418613 | .416785 | .414965 | .413151 | .411345 | .409547 | .407755 | .405971 |
| 2.2 | .404194 | .402424 | .400661 | .398906 | .397157 | .395416 | .393682 | .391955 | .390235 | .388522 |
| 2.3 | .386816 | .385117 | .383425 | .381740 | .380062 | .378390 | .376726 | .375068 | .373418 | .371774 |
| 2.4 | .370137 | .368507 | .366883 | .365266 | .363656 | .362053 | .360456 | .358866 | .357283 | .355706 |
| 2.5 | .354136 | .352572 | .351015 | .349465 | .347921 | .346383 | .344852 | .343328 | .341810 | .340298 |
| 2.6 | .338793 | .337294 | .335801 | .334315 | .332835 | .331361 | .329893 | .328432 | .326977 | .325528 |
| 2.7 | .324086 | .322649 | .321219 | .319795 | .318377 | .316965 | .315559 | .314159 | .312765 | .311377 |
| 2.8 | .309995 | .308619 | .307249 | .305885 | .304527 | .303174 | .301828 | .300487 | .299152 | .297823 |
| 2.9 | .296500 | .295182 | .293870 | .292564 | .291264 | .289969 | .288680 | .287397 | .286119 | .284847 |
| 3.0 | .283580 | .282319 | .281063 | .279813 | .278568 | .277329 | .276095 | .274867 | .273644 | .272427 |
| 3.1 | .271215 | .270008 | .268807 | .267610 | .266419 | .265234 | .264054 | .262879 | .261709 | .260544 |
| 3.2 | .259385 | .258230 | .257081 | .255937 | .254798 | .253664 | .252535 | .251412 | .250293 | .249179 |
| 3.3 | .248070 | .246966 | .245868 | .244774 | .243684 | .242600 | .241521 | .240447 | .239377 | .238312 |
| 3.4 | .237252 | .236197 | .235146 | .234101 | .233060 | .232023 | .230991 | .229964 | .228942 | .227924 |
| 3.5 | .226911 | .225903 | .224899 | .223899 | .222904 | .221914 | .220928 | .219947 | .218970 | .217998 |
| 3.6 | .217030 | .216066 | .215107 | .214152 | .213201 | .212255 | .211313 | .210376 | .209442 | .208513 |
| 3.7 | .207589 | .206668 | .205752 | .204840 | .203932 | .203028 | .202128 | .201233 | .200341 | .199454 |
| 3.8 | .198571 | .197692 | .196817 | .195945 | .195078 | .194215 | .193356 | .192501 | .191650 | .190803 |
| 3.9 | .189959 | .189120 | .188284 | .187452 | .186624 | .185800 | .184980 | .184164 | .183351 | .182542 |

$U/3RT$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 4.0 | 0.181737 | 0.180935 | 0.180138 | 0.179344 | 0.178553 | 0.177767 | 0.176984 | 0.176204 | 0.175428 | 0.174656 |
| 4.1 | .173888 | .173123 | .172361 | .171603 | .170849 | .170098 | .169351 | .168607 | .167866 | .167129 |
| 4.2 | .166396 | .165666 | .164939 | .164216 | .163496 | .162779 | .162066 | .161356 | .160649 | .159946 |
| 4.3 | .159246 | .158549 | .157856 | .157166 | .156479 | .155795 | .155114 | .154437 | .153763 | .153092 |
| 4.4 | .152424 | .151759 | .151097 | .150439 | .149783 | .149131 | .148482 | .147835 | .147192 | .146552 |
| 4.5 | .145914 | .145280 | .144649 | .144021 | .143395 | .142773 | .142153 | .141537 | .140923 | .140312 |
| 4.6 | .139704 | .139099 | .138497 | .137898 | .137301 | .136707 | .136116 | .135528 | .134943 | .134360 |
| 4.7 | .133780 | .133203 | .132628 | .132057 | .131488 | .130921 | .130357 | .129796 | .129238 | .128682 |
| 4.8 | .128129 | .127579 | .127031 | .126485 | .125942 | .125402 | .124864 | .124329 | .123797 | .123267 |
| 4.9 | .122739 | .122214 | .121691 | .121171 | .120653 | .120138 | .119625 | .119114 | .118606 | .118101 |
| 5.0 | .117598 | .117097 | .116598 | .116102 | .115608 | .115116 | .114627 | .114140 | .113656 | .113174 |
| 5.1 | .112694 | .112216 | .111740 | .111267 | .110796 | .110327 | .109861 | .109396 | .108934 | .108474 |
| 5.2 | .108016 | .107561 | .107107 | .106656 | .106206 | .105759 | .105314 | .104871 | .104430 | .103992 |
| 5.3 | .103555 | .103120 | .102688 | .102257 | .101829 | .101402 | .100978 | .100555 | .100135 | .0997163 |
| 5.4 | .0992997 | .0988852 | .0984726 | .0980619 | .0976531 | .0972463 | .0968414 | .0964384 | .0960373 | .0956381 |
| 5.5 | .0952408 | .0948453 | .0944517 | .0940600 | .0936701 | .0932821 | .0928958 | .0925114 | .0921288 | .0917480 |
| 5.6 | .0913690 | .0909917 | .0906162 | .0902425 | .0898706 | .0895004 | .0891319 | .0887652 | .0884002 | .0880369 |
| 5.7 | .0876753 | .0873155 | .0869573 | .0866007 | .0862459 | .0858927 | .0855412 | .0851913 | .0848431 | .0844965 |
| 5.8 | .0841515 | .0838082 | .0834664 | .0831263 | .0827877 | .0824508 | .0821154 | .0817815 | .0814493 | .0811186 |
| 5.9 | .0807894 | .0804618 | .0801357 | .0798112 | .0794881 | .0791666 | .0788466 | .0785280 | .0782110 | .0778954 |

*U/3RT*

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 6.0 | 0.0775813 | 0.0772687 | 0.0769575 | 0.0766478 | 0.0763395 | 0.0760327 | 0.0757273 | 0.0754233 | 0.0751208 | 0.0748196 |
| 6.1 | .0745198 | .0742215 | .0739245 | .0736289 | .0733347 | .0730419 | .0727504 | .0724603 | .0721715 | .0718841 |
| 6.2 | .0715980 | .0713132 | .0710297 | .0707476 | .0704668 | .0701873 | .0699090 | .0696321 | .0693564 | .0690821 |
| 6.3 | .0688090 | .0685371 | .0682665 | .0679972 | .0677291 | .0674623 | .0671967 | .0669323 | .0666691 | .0664072 |
| 6.4 | .0661465 | .0658869 | .0656286 | .0653715 | .0651155 | .0648607 | .0646071 | .0643547 | .0641034 | .0638533 |
| 6.5 | .0636043 | .0633565 | .0631098 | .0628643 | .0626199 | .0623766 | .0621344 | .0618934 | .0616534 | .0614146 |
| 6.6 | .0611768 | .0609402 | .0607046 | .0604701 | .0602366 | .0600043 | .0597730 | .0595428 | .0593136 | .0590854 |
| 6.7 | .0588583 | .0586323 | .0584073 | .0581833 | .0579603 | .0577384 | .0575174 | .0572975 | .0570785 | .0568606 |
| 6.8 | .0566437 | .0564277 | .0562127 | .0559987 | .0557857 | .0555737 | .0553626 | .0551525 | .0549433 | .0547351 |
| 6.9 | .0545278 | .0543214 | .0541160 | .0539115 | .0537080 | .0535053 | .0533036 | .0531028 | .0529029 | .0527039 |
| 7.0 | .0525059 | .0523087 | .0521123 | .0519169 | .0517224 | .0515287 | .0513359 | .0511440 | .0509530 | .0507628 |
| 7.1 | .0505734 | .0503849 | .0501973 | .0500105 | .0498245 | .0496394 | .0494551 | .0492716 | .0490890 | .0489071 |
| 7.2 | .0487261 | .0485459 | .0483665 | .0481879 | .0480101 | .0478331 | .0476569 | .0474815 | .0473068 | .0471329 |
| 7.3 | .0469598 | .0467875 | .0466160 | .0464452 | .0462752 | .0461059 | .0459374 | .0457696 | .0456026 | .0454363 |
| 7.4 | .0452707 | .0451059 | .0449418 | .0447785 | .0446158 | .0444539 | .0442927 | .0441322 | .0439725 | .0438134 |
| 7.5 | .0436550 | .0434974 | .0433404 | .0431841 | .0430285 | .0428736 | .0427194 | .0425658 | .0424129 | .0422607 |
| 7.6 | .0421092 | .0419583 | .0418081 | .0416586 | .0415097 | .0413615 | .0412139 | .0410669 | .0409206 | .0407750 |
| 7.7 | .0406299 | .0404855 | .0403418 | .0401987 | .0400562 | .0399143 | .0397730 | .0396323 | .0394923 | .0393529 |
| 7.8 | .0392140 | .0390758 | .0389382 | .0388011 | .0386647 | .0385289 | .0383936 | .0382590 | .0381249 | .0379914 |
| 7.9 | .0378584 | .0377261 | .0375943 | .0374631 | .0373324 | .0372023 | .0370728 | .0369439 | .0368155 | .0366876 |

$U/3RT$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 8.0 | 0.0365603 | 0.0364335 | 0.0363073 | 0.0361816 | 0.0360565 | 0.0359319 | 0.0358078 | 0.0356843 | 0.0355613 | 0.0354388 |
| 8.1 | .0353169 | .0351954 | .0350745 | .0349541 | .0348342 | .0347149 | .0345960 | .0344776 | .0343598 | .0342424 |
| 8.2 | .0341256 | .0340092 | .0338933 | .0337780 | .0336631 | .0335487 | .0334348 | .0333213 | .0332084 | .0330959 |
| 8.3 | .0329839 | .0328724 | .0327613 | .0326507 | .0325406 | .0324310 | .0323218 | .0322130 | .0321048 | .0319970 |
| 8.4 | .0318896 | .0317827 | .0316762 | .0315702 | .0314646 | .0313594 | .0312547 | .0311505 | .0310467 | .0309433 |
| 8.5 | .0308403 | .0307378 | .0306357 | .0305340 | .0304328 | .0303319 | .0302315 | .0301315 | .0300319 | .0299328 |
| 8.6 | .0298340 | .0297357 | .0296378 | .0295402 | .0294431 | .0293464 | .0292500 | .0291541 | .0290586 | .0289634 |
| 8.7 | .0288687 | .0287744 | .0286804 | .0285868 | .0284936 | .0284008 | .0283084 | .0282163 | .0281247 | .0280334 |
| 8.8 | .0279424 | .0278519 | .0277617 | .0276719 | .0275825 | .0274934 | .0274047 | .0273163 | .0272283 | .0271407 |
| 8.9 | .0270534 | .0269665 | 0268799 | .0267937 | .0267078 | .0266223 | .0265371 | .0264523 | .0263678 | .0262837 |
| 9.0 | .0261999 | .0261164 | .0260333 | .0259505 | .0258681 | .0257859 | .0257041 | .0256227 | .0255416 | .0254608 |
| 9.1 | .0253803 | .0253001 | .0252203 | .0251408 | .0250616 | .0249827 | .0249041 | .0248259 | .0247479 | .0246703 |
| 9.2 | .0245930 | .0245160 | .0244393 | .0243629 | .0242868 | .0242110 | .0241355 | .0240603 | .0239854 | .0239108 |
| 9.3 | .0238365 | .0237625 | .0236888 | .0236154 | .0235423 | .0234694 | .0233969 | .0233246 | .0232526 | .0231809 |
| 9.4 | .0231095 | .0230384 | .0229676 | .0228970 | .0228267 | .0227567 | .0226869 | .0226174 | .0225482 | .0224793 |
| 9.5 | .0224107 | .0223423 | .0222741 | .0222063 | .0221387 | .0220714 | .0220043 | .0219375 | .0218709 | .0218046 |
| 9.6 | .0217386 | .0216728 | .0216073 | .0215421 | .0214771 | .0214123 | .0213478 | .0212835 | .0212195 | .0211558 |
| 9.7 | .0210923 | .0210290 | .0209659 | .0209031 | .0208406 | .0207783 | .0207162 | .0206544 | .0205928 | .0205315 |
| 9.8 | .0204704 | .0204095 | .0203488 | .0202884 | .0202282 | .0201683 | .0201085 | .0200490 | .0199897 | .0199307 |
| 9.9 | .0198719 | .0198133 | .0197549 | .0196967 | .0196388 | .0195811 | .0195236 | .0194663 | .0194092 | .0193524 |

U/3RT

| x | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 10.0 | 0.0192958 | 0.0192393 | 0.0191831 | 0.0191271 | 0.0190714 | 0.0190158 | 0.0189604 | 0.0189053 | 0.0188503 | 0.0187956 |
| 10.1 | .0187410 | .0186867 | .0186326 | .0185787 | .0185249 | .0184714 | .0184181 | .0183650 | .0183120 | .0182593 |
| 10.2 | .0182068 | .0181544 | .0181023 | .0180504 | .0179986 | .0179470 | .0178957 | .0178445 | .0177935 | .0177427 |
| 10.3 | .0176921 | .0176416 | .0175914 | .0175413 | .0174915 | .0174418 | .0173923 | .0173430 | .0172938 | .0172449 |
| 10.4 | .0171961 | .0171475 | .0170991 | .0170508 | .0170027 | .0169548 | .0169071 | .0168596 | .0168122 | .0167650 |
| 10.5 | .0167180 | .0166711 | .0166244 | .0165779 | .0165316 | .0164854 | .0164394 | .0163936 | .0163479 | .0163024 |
| 10.6 | .0162570 | .0162118 | .0161668 | .0161220 | .0160773 | .0160328 | .0159884 | .0159442 | .0159001 | .0158562 |
| 10.7 | .0158125 | .0157689 | .0157255 | .0156822 | .0156391 | .0155962 | .0155534 | .0155107 | .0154682 | .0154259 |
| 10.8 | .0153837 | .0153416 | .0152997 | .0152580 | .0152164 | .0151749 | .0151336 | .0150925 | .0150515 | .0150106 |
| 10.9 | .0149699 | .0149293 | .0148889 | .0148486 | .0148084 | .0147684 | .0147286 | .0146888 | .0146492 | .0146098 |
| 11.0 | .0145705 | .0145313 | .0144923 | .0144534 | .0144146 | .0143760 | .0143375 | .0142992 | .0142610 | .0142229 |
| 11.1 | .0141849 | .0141471 | .0141094 | .0140719 | .0140345 | .0139972 | .0139600 | .0139230 | .0138861 | .0138493 |
| 11.2 | .0138126 | .0137761 | .0137397 | .0137034 | .0136673 | .0136313 | .0135954 | .0135596 | .0135239 | .0134884 |
| 11.3 | .0134530 | .0134177 | .0133826 | .0133475 | .0133126 | .0132778 | .0132431 | .0132085 | .0131741 | .0131398 |
| 11.4 | .0131056 | .0130715 | .0130375 | .0130036 | .0129699 | .0129362 | .0129027 | .0128693 | .0128360 | .0128029 |
| 11.5 | .0127698 | .0127368 | .0127040 | .0126713 | .0126387 | .0126061 | .0125737 | .0125415 | .0125093 | .0124772 |
| 11.6 | .0124452 | .0124134 | .0123816 | .0123500 | .0123184 | .0122870 | .0122557 | .0122245 | .0121934 | .0121623 |
| 11.7 | .0121314 | .0121006 | .0120699 | .0120393 | .0120088 | .0119784 | .0119481 | .0119179 | .0118878 | .0118578 |
| 11.8 | .0118279 | .0117982 | .0117685 | .0117389 | .0117094 | .0116799 | .0116506 | .0116214 | .0115923 | .0115633 |
| 11.9 | .0115344 | .0115055 | .0114768 | .0114482 | .0114196 | .0113912 | .0113628 | .0113346 | .0113064 | .0112783 |

*U*/3*RT*

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 12.0 | 0.0112503 | 0.0112224 | 0.0111946 | 0.0111669 | 0.0111393 | 0.0111118 | 0.0110843 | 0.0110570 | 0.0110297 | 0.0110025 |
| 12.1 | .0109754 | .0109484 | .0109215 | .0108947 | .0108679 | .0108413 | .0108147 | .0107882 | .0107618 | .0107355 |
| 12.2 | .0107093 | .0106832 | .0106571 | .0106311 | .0106052 | .0105794 | .0105537 | .0105281 | .0105025 | .0104770 |
| 12.3 | .0104516 | .0104263 | .0104011 | .0103759 | .0103509 | .0103259 | .0103010 | .0102761 | .0102514 | .0102267 |
| 12.4 | .0102021 | .0101776 | .0101531 | .0101288 | .0101045 | .0100803 | .0100561 | .0100321 | .0100081 | .00998419 |
| 12.5 | .00996036 | .00993661 | .00991293 | .00988932 | .00986579 | .00984233 | .00981895 | .00979564 | .00977240 | .00974923 |
| 12.6 | .00972614 | .00970312 | .00968017 | .00965730 | .00963449 | .00961176 | .00958909 | .00956650 | .00954398 | .00952153 |
| 12.7 | .00949915 | .00947683 | .00945459 | .00943241 | .00941031 | .00938827 | .00936630 | .00934440 | .00932257 | .00930080 |
| 12.8 | .00927910 | .00925747 | .00923591 | .00921441 | .00919298 | .00917161 | .00915031 | .00912907 | .00910790 | .00908680 |
| 12.9 | .00906576 | .00904478 | .00902387 | .00900302 | .00898224 | .00896152 | .00894086 | .00892027 | .00889974 | .00887927 |
| 13.0 | .00885886 | .00883851 | .00881823 | .00879801 | .00877785 | .00875775 | .00873771 | .00871774 | .00869782 | .00867796 |
| 13.1 | .00865817 | .00863843 | .00861875 | .00859914 | .00857958 | .00856008 | .00854064 | .00852125 | .00850193 | .00848266 |
| 13.2 | .00846345 | .00844430 | .00842521 | .00840617 | .00838719 | .00836827 | .00834941 | .00833060 | .00831184 | .00829314 |
| 13.3 | .00827450 | .00825592 | .00823739 | .00821891 | .00820049 | .00818212 | .00816381 | .00814555 | .00812735 | .00810920 |
| 13.4 | .00809111 | .00807306 | .00805507 | .00803714 | .00801926 | .00800143 | .00798365 | .00796592 | .00794825 | .00793063 |
| 13.5 | .00791306 | .00789554 | .00787807 | .00786066 | .00784330 | .00782598 | .00780872 | .00779151 | .00777435 | .00775724 |
| 13.6 | .00774017 | .00772316 | .00770620 | .00768929 | .00767242 | .00765561 | .00763884 | .00762213 | .00760546 | .00758884 |
| 13.7 | .00757226 | .00755574 | .00753927 | .00752284 | .00750646 | .00749012 | .00747384 | .00745760 | .00744140 | .00742526 |
| 13.8 | .00740916 | .00739310 | .00737710 | .00736114 | .00734522 | .00732935 | .00731353 | .00729775 | .00728201 | .00726632 |
| 13.9 | .00725068 | .00723508 | .00721953 | .00720402 | .00718855 | .00717313 | .00715775 | .00714242 | .00712713 | .00711188 |

| x | U/3RT<br>0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 14.0 | 0.00709668 | 0.00708152 | 0.00706640 | 0.00705132 | 0.00703629 | 0.00702130 | 0.00700636 | 0.00699145 | 0.00697659 | 0.00696177 |
| 14.1 | .00694699 | .00693225 | .00691755 | .00690290 | .00688829 | .00687371 | .00685918 | .00684469 | .00683024 | .00681583 |
| 14.2 | .00680146 | .00678713 | .00677285 | .00675860 | .00674439 | .00673022 | .00671609 | .00670200 | .00668795 | .00667394 |
| 14.3 | .00665996 | .00664603 | .00663213 | .00661828 | .00660446 | .00659068 | .00657694 | .00656323 | .00654957 | .00653594 |
| 14.4 | .00652235 | .00650880 | .00649528 | .00648180 | .00646836 | .00645496 | .00644159 | .00642826 | .00641497 | .00640171 |
| 14.5 | .00638849 | .00637531 | .00636216 | .00634905 | .00633597 | .00632293 | .00630992 | .00629695 | .00628402 | .00627112 |
| 14.6 | .00625826 | .00624543 | .00623264 | .00621988 | .00620716 | .00619447 | .00618181 | .00616919 | .00615661 | .00614405 |
| 14.7 | .00613153 | .00611905 | .00610660 | .00609418 | .00608180 | .00606945 | .00605714 | .00604485 | .00603260 | .00602039 |
| 14.8 | .00600820 | .00599605 | .00598393 | .00597185 | .00595979 | .00594777 | .00593578 | .00592383 | .00591190 | .00590001 |
| 14.9 | .00588815 | .00587632 | .00586452 | .00585275 | .00584102 | .00582932 | .00581764 | .00580600 | .00579439 | .00578281 |
| 15.0 | .00577126 | .00575975 | .00574826 | .00573680 | .00572537 | .00571398 | .00570261 | .00569128 | .00567997 | .00566869 |
| 15.1 | .00565745 | .00564623 | .00563504 | .00562388 | .00561276 | .00560166 | .00559059 | .00557955 | .00556853 | .00555755 |
| 15.2 | .00554660 | .00553567 | .00552478 | .00551391 | .00550307 | .00549226 | .00548147 | .00547072 | .00545999 | .00544929 |
| 15.3 | .00543862 | .00542798 | .00541736 | .00540677 | .00539621 | .00538568 | .00537518 | .00536470 | .00535425 | .00534382 |
| 15.4 | .00533342 | .00532305 | .00531271 | .00530239 | .00529210 | .00528184 | .00527160 | .00526139 | .00525121 | .00524105 |
| 15.5 | .00523092 | .00522081 | .00521073 | .00520068 | .00519065 | .00518065 | .00517067 | .00516072 | .00515080 | .00514090 |
| 15.6 | .00513102 | .00512117 | .00511135 | .00510155 | .00509177 | .00508202 | .00507230 | .00506260 | .00505292 | .00504327 |
| 15.7 | .00503365 | .00502405 | .00501447 | .00500492 | .00499539 | .00498588 | .00497640 | .00496694 | .00495751 | .00494810 |
| 15.8 | .00493872 | .00492936 | .00492002 | .00491070 | .00490141 | .00489215 | .00488290 | .00487368 | .00486448 | .00485531 |
| 15.9 | .00484616 | .00483703 | .00482792 | .00481884 | .00480978 | .00480074 | .00479173 | .00478274 | .00477377 | .00476482 |

$U/3RT$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 16.0 | 0.00475589 | 0.00474699 | 0.00473811 | 0.00472925 | 0.00472042 | 0.00471160 | 0.00470281 | 0.00469404 | 0.00468529 | 0.00467656 |
| 16.1 | .00466786 | .00465917 | .00465051 | .00464187 | .00463325 | .00462465 | .00461607 | .00460752 | .00459898 | .00459047 |
| 16.2 | .00458198 | .00457350 | .00456505 | .00455662 | .00454821 | .00453982 | .00453146 | .00452311 | .00451478 | .00450647 |
| 16.3 | .00449819 | .00448992 | .00448167 | .00447345 | .00446524 | .00445706 | .00444889 | .00444075 | .00443262 | .00442451 |
| 16.4 | .00441643 | .00440836 | .00440031 | .00439229 | .00438428 | .00437629 | .00436832 | .00436037 | .00435244 | .00434453 |
| 16.5 | .00433664 | .00432876 | .00432091 | .00431307 | .00430526 | .00429746 | .00428968 | .00428192 | .00427418 | .00426646 |
| 16.6 | .00425875 | .00425107 | .00424340 | .00423575 | .00422812 | .00422051 | .00421292 | .00420534 | .00419778 | .00419024 |
| 16.7 | .00418272 | .00417522 | .00416774 | .00416027 | .00415282 | .00414539 | .00413797 | .00413058 | .00412320 | .00411584 |
| 16.8 | .00410849 | .00410117 | .00409386 | .00408656 | .00407929 | .00407203 | .00406479 | .00405757 | .00405037 | .00404318 |
| 16.9 | .00403601 | .00402885 | .00402171 | .00401459 | .00400749 | .00400040 | .00399333 | .00398628 | .00397924 | .00397222 |
| 17.0 | .00396521 | .00395822 | .00395125 | .00394430 | .00393736 | .00393044 | .00392353 | .00391664 | .00390977 | .00390291 |
| 17.1 | .00389606 | .00388924 | .00388243 | .00387563 | .00386885 | .00386209 | .00385535 | .00384862 | .00384190 | .00383520 |
| 17.2 | .00382852 | .00382185 | .00381519 | .00380855 | .00380193 | .00379532 | .00378873 | .00378216 | .00377560 | .00376905 |
| 17.3 | .00376252 | .00375600 | .00374950 | .00374301 | .00373654 | .00373009 | .00372365 | .00371722 | .00371081 | .00370441 |
| 17.4 | .00369803 | .00369166 | .00368531 | .00367897 | .00367264 | .00366633 | .00366004 | .00365376 | .00364749 | .00364124 |
| 17.5 | .00363500 | .00362878 | .00362257 | .00361637 | .00361019 | .00360403 | .00359787 | .00359173 | .00358561 | .00357950 |
| 17.6 | .00357340 | .00356732 | .00356125 | .00355519 | .00354915 | .00354312 | .00353711 | .00353110 | .00352512 | .00351914 |
| 17.7 | .00351318 | .00350723 | .00350130 | .00349538 | .00348947 | .00348358 | .00347770 | .00347183 | .00346598 | .00346014 |
| 17.8 | .00345431 | .00344849 | .00344269 | .00343690 | .00343113 | .00342536 | .00341961 | .00341388 | .00340815 | .00340244 |
| 17.9 | .00339674 | .00339106 | .00338538 | .00337972 | .00337408 | .00336844 | .00336282 | .00335721 | .00335161 | .00334602 |

$U/3RT$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 18.0 | 0.00334045 | 0.00333489 | 0.00332934 | 0.00332380 | 0.00331828 | 0.00331277 | 0.00330727 | 0.00330178 | 0.00329631 | 0.00329084 |
| 18.1 | .00328539 | .00327995 | .00327453 | .00326911 | .00326371 | .00325832 | .00325294 | .00324757 | .00324221 | .00323687 |
| 18.2 | .00323154 | .00322622 | .00322091 | .00321561 | .00321033 | .00320505 | .00319979 | .00319454 | .00318930 | .00318407 |
| 18.3 | .00317886 | .00317365 | .00316846 | .00316327 | .00315810 | .00315294 | .00314779 | .00314266 | .00313753 | .00313241 |
| 18.4 | .00312731 | .00312222 | .00311714 | .00311206 | .00310700 | .00310196 | .00309692 | .00309189 | .00308687 | .00308187 |
| 18.5 | .00307687 | .00307189 | .00306692 | .00306195 | .00305700 | .00305206 | .00304713 | .00304221 | .00303730 | .00303240 |
| 18.6 | .00302752 | .00302264 | .00301777 | .00301291 | .00300807 | .00300323 | .00299841 | .00299359 | .00298879 | .00298399 |
| 18.7 | .00297921 | .00297443 | .00296967 | .00296492 | .00296017 | .00295544 | .00295072 | .00294600 | .00294130 | .00293661 |
| 18.8 | .00293192 | .00292725 | .00292258 | .00291793 | .00291329 | .00290865 | .00290403 | .00289942 | .00289481 | .00289022 |
| 18.9 | .00288563 | .00288106 | .00287649 | .00287193 | .00286739 | .00286285 | .00285832 | .00285381 | .00284930 | .00284480 |
| 19.0 | .00284031 | .00283583 | .00283136 | .00282690 | .00282245 | .00281800 | .00281357 | .00280915 | .00280473 | .00280033 |
| 19.1 | .00279593 | .00279155 | .00278717 | .00278280 | .00277844 | .00277409 | .00276975 | .00276542 | .00276109 | .00275678 |
| 19.2 | .00275247 | .00274818 | .00274389 | .00273961 | .00273534 | .00273108 | .00272683 | .00272259 | .00271835 | .00271413 |
| 19.3 | .00270991 | .00270570 | .00270151 | .00269732 | .00269313 | .00268896 | .00268480 | .00268064 | .00267649 | .00267235 |
| 19.4 | .00266822 | .00266410 | .00265999 | .00265588 | .00265179 | .00264770 | .00264362 | .00263955 | .00263549 | .00263143 |
| 19.5 | .00262738 | .00262335 | .00261932 | .00261530 | .00261128 | .00260728 | .00260328 | .00259929 | .00259531 | .00259134 |
| 19.6 | .00258738 | .00258342 | .00257947 | .00257553 | .00257160 | .00256768 | .00256376 | .00255985 | .00255595 | .00255206 |
| 19.7 | .00254817 | .00254430 | .00254043 | .00253657 | .00253272 | .00252887 | .00252503 | .00252120 | .00251738 | .00251357 |
| 19.8 | .00250976 | .00250596 | .00250217 | .00249839 | .00249461 | .00249084 | .00248708 | .00248333 | .00247958 | .00247585 |
| 19.9 | .00247212 | .00246839 | .00246468 | .00246097 | .00245727 | .00245358 | .00244989 | .00244621 | .00244254 | .00243888 |

$U/3RT$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 20.0 | 0.00243522 | 0.00243157 | 0.00242793 | 0.00242429 | 0.00242067 | 0.00241705 | 0.00241343 | 0.00240983 | 0.00240623 | 0.00240264 |
| 20.1 | .00239905 | .00239548 | .00239191 | .00238834 | .00238479 | .00238124 | .00237770 | .00237416 | .00237064 | .00236712 |
| 20.2 | .00236360 | .00236010 | .00235660 | .00235310 | .00234962 | .00234614 | .00234266 | .00233920 | .00233574 | .00233229 |
| 20.3 | .00232884 | .00232540 | .00232197 | .00231855 | .00231513 | .00231172 | .00230832 | .00230492 | .00230153 | .00229814 |
| 20.4 | .00229476 | .00229139 | .00228803 | .00228467 | .00228132 | .00227797 | .00227463 | .00227130 | .00226798 | .00226466 |
| 20.5 | .00226135 | .00225804 | .00225474 | .00225145 | .00224816 | .00224488 | .00224161 | .00223834 | .00223508 | .00223182 |
| 20.6 | .00222857 | .00222533 | .00222210 | .00221887 | .00221564 | .00221242 | .00220921 | .00220601 | .00220281 | .00219962 |
| 20.7 | .00219643 | .00219325 | .00219008 | .00218691 | .00218375 | .00218059 | .00217744 | .00217430 | .00217116 | .00216803 |
| 20.8 | .00216491 | .00216179 | .00215867 | .00215556 | .00215246 | .00214937 | .00214628 | .00214319 | .00214012 | .00213705 |
| 20.9 | .00213398 | .00213092 | .00212786 | .00212481 | .00212177 | .00211874 | .00211571 | .00211268 | .00210966 | .00210665 |
| 21.0 | .00210364 | .00210064 | .00209764 | .00209465 | .00209166 | .00208868 | .00208571 | .00208274 | .00207978 | .00207682 |
| 21.1 | .00207387 | .00207092 | .00206798 | .00206505 | .00206212 | .00205920 | .00205628 | .00205337 | .00205046 | .00204756 |
| 21.2 | .00204466 | .00204177 | .00203889 | .00203601 | .00203313 | .00203026 | .00202740 | .00202454 | .00202169 | .00201884 |
| 21.3 | .00201600 | .00201316 | .00201033 | .00200750 | .00200468 | .00200187 | .00199906 | .00199625 | .00199345 | .00199066 |
| 21.4 | .00198787 | .00198509 | .00198231 | .00197953 | .00197676 | .00197400 | .00197124 | .00196849 | .00196574 | .00196300 |
| 21.5 | .00196026 | .00195753 | .00195480 | .00195208 | .00194936 | .00194665 | .00194394 | .00194124 | .00193854 | .00193585 |
| 21.6 | .00193316 | .00193048 | .00192780 | .00192513 | .00192246 | .00191980 | .00191714 | .00191449 | .00191184 | .00190920 |
| 21.7 | .00190656 | .00190393 | .00190130 | .00189867 | .00189605 | .00189344 | .00189083 | .00188823 | .00188563 | .00188303 |
| 21.8 | .00188044 | .00187786 | .00187528 | .00187270 | .00187013 | .00186756 | .00186500 | .00186244 | .00185989 | .00185734 |
| 21.9 | .00185480 | .00185226 | .00184973 | .00184720 | .00184467 | .00184215 | .00183964 | .00183713 | .00183462 | .00183212 |

*U*/3*RT*

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 22.0 | 0.00182962 | 0.00182713 | 0.00182464 | 0.00182216 | 0.00181968 | 0.00181720 | 0.00181473 | 0.00181227 | 0.00180981 | 0.00180735 |
| 22.1 | .00180490 | .00180245 | .00180001 | .00179757 | .00179513 | .00179270 | .00179028 | .00178786 | .00178544 | .00178303 |
| 22.2 | .00178062 | .00177821 | .00177581 | .00177342 | .00177103 | .00176864 | .00176626 | .00176388 | .00176150 | .00175913 |
| 22.3 | .00175677 | .00175441 | .00175205 | .00174970 | .00174735 | .00174501 | .00174267 | .00174033 | .00173800 | .00173567 |
| 22.4 | .00173335 | .00173103 | .00172871 | .00172640 | .00172409 | .00172179 | .00171949 | .00171720 | .00171491 | .00171262 |
| 22.5 | .00171034 | .00170806 | .00170578 | .00170351 | .00170125 | .00169899 | .00169673 | .00169447 | .00169222 | .00168998 |
| 22.6 | .00168774 | .00168550 | .00168326 | .00168103 | .00167880 | .00167658 | .00167436 | .00167215 | .00166994 | .00166773 |
| 22.7 | .00166553 | .00166333 | .00166113 | .00165894 | .00165675 | .00165457 | .00165239 | .00165021 | .00164804 | .00164587 |
| 22.8 | .00164371 | .00164155 | .00163939 | .00163724 | .00163509 | .00163294 | .00163080 | .00162866 | .00162653 | .00162440 |
| 22.9 | .00162227 | .00162015 | .00161803 | .00161591 | .00161380 | .00161169 | .00160958 | .00160748 | .00160539 | .00160329 |
| 23.0 | .00160120 | .00159911 | .00159703 | .00159495 | .00159288 | .00159080 | .00158873 | .00158667 | .00158461 | .00158255 |
| 23.1 | .00158050 | .00157845 | .00157640 | .00157435 | .00157231 | .00157028 | .00156824 | .00156621 | .00156419 | .00156217 |
| 23.2 | .00156015 | .00155813 | .00155612 | .00155411 | .00155210 | .00155010 | .00154810 | .00154611 | .00154412 | .00154213 |
| 23.3 | .00154014 | .00153816 | .00153619 | .00153421 | .00153224 | .00153027 | .00152831 | .00152635 | .00152439 | .00152243 |
| 23.4 | .00152048 | .00151854 | .00151659 | .00151465 | .00151271 | .00151078 | .00150885 | .00150692 | .00150499 | .00150307 |
| 23.5 | .00150116 | .00149924 | .00149733 | .00149542 | .00149352 | .00149162 | .00148972 | .00148782 | .00148593 | .00148404 |
| 23.6 | .00148215 | .00148027 | .00147839 | .00147652 | .00147464 | .00147277 | .00147091 | .00146904 | .00146718 | .00146533 |
| 23.7 | .00146347 | .00146162 | .00145977 | .00145793 | .00145609 | .00145425 | .00145241 | .00145058 | .00144875 | .00144693 |
| 23.8 | .00144510 | .00144328 | .00144147 | .00143965 | .00143784 | .00143603 | .00143423 | .00143243 | .00143063 | .00142883 |
| 23.9 | .00142704 | .00142525 | .00142346 | .00142168 | .00141990 | .00141812 | .00141634 | .00141457 | .00141280 | .00141104 |
| 24.0 | .00140928 | | | | | | | | | |

$$\frac{U}{3RT}=\frac{19.481818}{x^3}\text{ when } x>24$$

## TABLE II

## DEBYE SPECIFIC HEAT FUNCTION

$$\frac{C_v}{3R}=\frac{12}{x^3}\left(\int_0^x \frac{y^3dy}{e^y-1}-\frac{3x}{e^x-1}\right)$$

$C_v/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.0 | 1.000000 | 0.999995 | 0.999980 | 0.999955 | 0.999920 | 0.999875 | 0.999820 | 0.999755 | 0.999680 | 0.999595 |
| 0.1 | .999500 | .999395 | .999280 | .999156 | .999021 | .998876 | .998721 | .998556 | .998382 | .998197 |
| 0.2 | .998003 | .997798 | .997584 | .997360 | .997126 | .996882 | .996628 | .996364 | .996091 | .995808 |
| 0.3 | .995514 | .995211 | .994899 | .994576 | .994244 | .993902 | .993550 | .993188 | .992817 | .992436 |
| 0.4 | .992045 | .991645 | .991235 | .990816 | .990387 | .989948 | .989500 | .989042 | .988574 | .988097 |
| 0.5 | .987611 | .987115 | .986610 | .986095 | .985571 | .985037 | .984494 | .983942 | .983380 | .982809 |
| 0.6 | .982229 | .981639 | .981041 | .980433 | .979816 | .979190 | .978554 | .977910 | .977256 | .976594 |
| 0.7 | .975922 | .975242 | .974552 | .973854 | .973147 | .972430 | .971705 | .970971 | .970229 | .969477 |
| 0.8 | .968717 | .967948 | .967171 | .966385 | .965590 | .964787 | .963975 | .963155 | .962326 | .961489 |
| 0.9 | .960643 | .959789 | .958927 | .958056 | .957177 | .956290 | .955395 | .954491 | .953580 | .952660 |
| 1.0 | .951732 | .950796 | .949853 | .948901 | .947941 | .946974 | .945999 | .945016 | .944025 | .943026 |
| 1.1 | .942020 | .941006 | .939985 | .938956 | .937919 | .936875 | .935824 | .934765 | .933699 | .932626 |
| 1.2 | .931545 | .930457 | .929362 | .928259 | .927150 | .926033 | .924910 | .923779 | .922642 | .921498 |
| 1.3 | .920346 | .919188 | .918024 | .916852 | .915674 | .914489 | .913298 | .912100 | .910895 | .909684 |
| 1.4 | 908467 | .907243 | .906013 | .904777 | .903534 | .902286 | .901031 | .899770 | .898503 | .897230 |
| 1.5 | 895951 | .894666 | .893375 | .892078 | .890775 | .889467 | .888153 | .886834 | .885509 | .884178 |
| 1.6 | .882842 | .881500 | .880153 | .878800 | .877442 | .876079 | .874711 | .873337 | .871959 | .870575 |
| 1.7 | .869186 | .867792 | .866394 | .864990 | .863581 | .862168 | .860750 | .859327 | .857900 | .856468 |
| 1.8 | .855031 | .853590 | .852144 | .850694 | .849239 | .847780 | .846317 | .844850 | .843378 | .841902 |
| 1.9 | .840423 | .838939 | .837451 | .835959 | .834463 | .832963 | .831460 | .829952 | .828441 | .826926 |

$C_v/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 2.0 | 0.825408 | 0.823886 | 0.822361 | 0.820832 | 0.819299 | 0.817763 | 0.816224 | 0.814681 | 0.813135 | 0.811586 |
| 2.1 | .810034 | .808479 | .806920 | .805359 | .803794 | .802227 | .800656 | .799083 | .797507 | .795928 |
| 2.2 | .794347 | .792763 | .791176 | .789586 | .787994 | .786400 | .784803 | .783203 | .781602 | .779998 |
| 2.3 | .778391 | .776783 | .775172 | .773559 | .771944 | .770327 | .768708 | .767087 | .765464 | .763839 |
| 2.4 | .762212 | .760584 | .758954 | .757322 | .755688 | .754053 | .752416 | .750777 | .749137 | .747496 |
| 2.5 | .745853 | .744209 | .742563 | .740916 | .739268 | .737619 | .735968 | .734316 | .732664 | .731010 |
| 2.6 | .729355 | .727699 | .726042 | .724385 | .722726 | .721067 | .719407 | .717746 | .716084 | .714422 |
| 2.7 | .712759 | .711095 | .709431 | .707766 | .706101 | .704436 | .702770 | .701104 | .699437 | .697770 |
| 2.8 | .696103 | .694435 | .692768 | .691100 | .689432 | .687764 | .686096 | .684428 | .682760 | .681092 |
| 2.9 | .679424 | .677757 | .676089 | .674422 | .672754 | .671087 | .669421 | .667755 | .666089 | .664423 |
| 3.0 | .662758 | .661093 | .659429 | .657766 | .656103 | .654440 | .652778 | .651117 | .649456 | .647796 |
| 3.1 | .646137 | .644479 | .642821 | .641165 | .639509 | .637854 | .636200 | .634546 | .632894 | .631243 |
| 3.2 | .629593 | .627944 | .626296 | .624649 | .623003 | .621359 | .619715 | .618073 | .616432 | .614792 |
| 3.3 | .613154 | .611517 | .609881 | .608247 | .606614 | .604983 | .603353 | .601724 | .600097 | .598472 |
| 3.4 | .596848 | .595226 | .593605 | .591986 | .590369 | .588753 | .587139 | .585526 | .583916 | .582307 |
| 3.5 | .580700 | .579095 | .577491 | .575889 | .574290 | .572692 | .571096 | .569502 | .567910 | .566320 |
| 3.6 | .564732 | .563146 | .561562 | .559980 | .558400 | .556823 | .555247 | .553674 | .552102 | .550533 |
| 3.7 | .548966 | .547401 | .545839 | .544279 | .542721 | .541165 | .539611 | .538060 | .536511 | .534965 |
| 3.8 | .533421 | .531879 | .530340 | .528803 | .527268 | .525736 | .524207 | .522680 | .521155 | .519633 |
| 3.9 | .518113 | .516596 | .515082 | .513570 | .512061 | .510554 | .509050 | .507548 | .506049 | .504553 |

$C_v/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 4.0 | 0.503059 | 0.501568 | 0.500080 | 0.498595 | 0.497112 | 0.495632 | 0.494154 | 0.492679 | 0.491207 | 0.489738 |
| 4.1 | .488272 | .486808 | .485347 | .483889 | .482434 | .480982 | .479532 | .478086 | .476642 | .475201 |
| 4.2 | .473763 | .472328 | .470896 | .469466 | .468040 | .466616 | .465196 | .463778 | .462363 | .460952 |
| 4.3 | .459543 | .458137 | .456734 | .455334 | .453938 | .452544 | .451153 | .449765 | .448380 | .446999 |
| 4.4 | .445620 | .444244 | .442872 | .441502 | .440136 | .438772 | .437412 | .436055 | .434701 | .433350 |
| 4.5 | .432002 | .430657 | .429315 | .427976 | .426641 | .425308 | .423979 | .422653 | .421330 | .420010 |
| 4.6 | .418693 | .417380 | .416069 | .414762 | .413458 | .412157 | .410859 | .409565 | .408273 | .406985 |
| 4.7 | .405700 | .404418 | .403139 | .401864 | .400591 | .399322 | .398056 | .396794 | .395534 | .394278 |
| 4.8 | .393025 | .391775 | .390528 | .389284 | .388044 | .386807 | .385573 | .384342 | .383114 | .381890 |
| 4.9 | .380669 | .379451 | .378237 | .377025 | .375817 | .374612 | .373410 | .372211 | .371016 | .369824 |
| 5.0 | .368635 | .367449 | .366267 | .365087 | .363911 | .362738 | .361568 | .360402 | .359239 | .358079 |
| 5.1 | .356922 | .355768 | .354618 | .353470 | .352326 | .351186 | .350048 | .348913 | .347782 | .346654 |
| 5.2 | .345529 | .344408 | .343289 | .342174 | .341062 | .339953 | .338847 | .337744 | .336645 | .335549 |
| 5.3 | .334456 | .333366 | .332279 | .331195 | .330115 | .329038 | .327963 | .326892 | .325825 | .324760 |
| 5.4 | .323698 | .322640 | .321585 | .320533 | .319484 | .318438 | .317395 | .316355 | .315319 | .314285 |
| 5.5 | .313255 | .312228 | .311203 | .310182 | .309164 | .308149 | .307138 | .306129 | .305123 | .304121 |
| 5.6 | .303121 | .302125 | .301131 | .300141 | .299154 | .298169 | .297188 | .296210 | .295235 | .294262 |
| 5.7 | .293293 | .292327 | .291364 | .290404 | .289447 | .288493 | .287541 | .286593 | .285648 | .284706 |
| 5.8 | .283767 | .282830 | .281897 | .280967 | .280039 | .279115 | .278193 | .277275 | .276359 | .275446 |
| 5.9 | .274536 | .273629 | .272725 | .271824 | .270926 | .270031 | .269138 | .268249 | .267362 | .266478 |

$C_v/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 6.0 | 0.265597 | 0.264719 | 0.263843 | 0.262971 | 0.262101 | 0.261234 | 0.260370 | 0.259509 | 0.258651 | 0.257795 |
| 6.1 | .256943 | .256093 | .255246 | .254401 | .253559 | .252721 | .251885 | .251051 | .250221 | .249393 |
| 6.2 | .248568 | .247745 | .246926 | .246109 | .245295 | .244483 | .243674 | .242868 | .242065 | .241264 |
| 6.3 | .240466 | .239670 | .238878 | .238088 | .237300 | .236515 | .235733 | .234954 | .234177 | .233403 |
| 6.4 | .232631 | .231862 | .231095 | .230331 | .229570 | .228811 | .228055 | .227302 | .226551 | .225802 |
| 6.5 | .225056 | .224313 | .223572 | .222834 | .222098 | .221364 | .220633 | .219905 | .219179 | .218456 |
| 6.6 | .217735 | .217017 | .216301 | .215588 | .214877 | .214168 | .213462 | .212758 | .212057 | .211358 |
| 6.7 | .210662 | .209968 | .209276 | .208587 | .207900 | .207215 | .206533 | .205853 | .205176 | .204501 |
| 6.8 | .203828 | .203158 | .202490 | .201824 | .201161 | .200500 | .199841 | .199185 | .198530 | .197878 |
| 6.9 | .197229 | .196581 | .195936 | .195294 | .194653 | .194015 | .193379 | .192745 | .192113 | .191484 |
| 7.0 | .190856 | .190231 | .189609 | .188988 | .188370 | .187753 | .187139 | .186527 | .185917 | .185310 |
| 7.1 | .184704 | .184101 | .183500 | .182901 | .182304 | .181709 | .181116 | .180526 | .179937 | .179351 |
| 7.2 | .178766 | .178184 | .177604 | .177025 | .176449 | .175875 | .175303 | .174733 | .174165 | .173599 |
| 7.3 | .173035 | .172473 | .171913 | .171355 | .170799 | .170245 | .169693 | .169143 | .168595 | .168049 |
| 7.4 | .167505 | .166963 | .166422 | .165884 | .165347 | .164813 | .164280 | .163750 | .163221 | .162694 |
| 7.5 | .162169 | .161646 | .161124 | .160605 | .160087 | .159572 | .159058 | .158546 | .158036 | .157527 |
| 7.6 | .157021 | .156516 | .156013 | .155512 | .155013 | .154515 | .154020 | .153526 | .153034 | .152543 |
| 7.7 | .152055 | .151568 | .151083 | .150599 | .150118 | .149638 | .149160 | .148683 | .148209 | .147736 |
| 7.8 | .147264 | .146795 | .146327 | .145861 | .145396 | .144933 | .144472 | .144013 | .143555 | .143098 |
| 7.9 | .142644 | .142191 | .141740 | .141290 | .140842 | .140395 | .139951 | .139508 | .139066 | .138626 |

$C_v/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 8.0 | 0.138187 | 0.137750 | 0.137315 | 0.136881 | 0.136449 | 0.136019 | 0.135590 | 0.135162 | 0.134736 | 0.134312 |
| 8.1 | .133889 | .133468 | .133048 | .132630 | .132213 | .131798 | .131384 | .130972 | .130561 | .130152 |
| 8.2 | .129744 | .129338 | .128933 | .128529 | .128127 | .127727 | .127328 | .126930 | .126534 | .126139 |
| 8.3 | .125746 | .125354 | .124964 | .124575 | .124187 | .123801 | .123416 | .123032 | .122650 | .122270 |
| 8.4 | .121890 | .121512 | .121136 | .120761 | .120387 | .120014 | .119643 | .119273 | .118905 | .118538 |
| 8.5 | .118172 | .117807 | .117444 | .117082 | .116722 | .116362 | .116004 | .115648 | .115292 | .114938 |
| 8.6 | .114585 | .114234 | .113883 | .113534 | .113187 | .112840 | .112495 | .112151 | .111808 | .111466 |
| 8.7 | .111126 | .110787 | .110449 | .110113 | .109777 | .109443 | .109110 | .108778 | .108447 | .108118 |
| 8.8 | .107790 | .107463 | .107137 | .106812 | .106489 | .106166 | .105845 | .105525 | .105206 | .104888 |
| 8.9 | .104572 | .104256 | .103942 | .103628 | .103316 | .103005 | .102695 | .102387 | .102079 | .101773 |
| 9.0 | .101467 | .101163 | .100859 | .100557 | .100256 | .0999562 | .0996573 | .0993594 | .0990626 | .0987669 |
| 9.1 | .0984722 | .0981786 | .0978861 | .0975946 | .0973041 | .0970146 | .0967262 | .0964389 | .0961525 | .0958672 |
| 9.2 | .0955829 | .0952996 | .0950174 | .0947361 | .0944558 | .0941766 | .0938983 | .0936210 | .0933448 | .0930695 |
| 9.3 | .0927951 | .0925218 | .0922494 | .0919780 | .0917076 | .0914381 | .0911696 | .0909021 | .0906355 | .0903698 |
| 9.4 | .0901051 | .0898414 | .0895785 | .0893166 | .0890557 | .0887956 | .0885365 | .0882783 | .0880210 | .0877646 |
| 9.5 | .0875092 | .0872546 | .0870010 | .0867482 | .0864964 | .0862454 | .0859953 | .0857461 | .0854978 | .0852504 |
| 9.6 | .0850038 | .0847581 | .0845133 | .0842693 | .0840262 | .0837840 | .0835426 | .0833020 | .0830623 | .0828235 |
| 9.7 | .0825855 | .0823483 | .0821120 | .0818765 | .0816418 | .0814080 | .0811750 | .0809428 | .0807114 | .0804808 |
| 9.8 | .0802510 | .0800221 | .0797939 | .0795666 | .0793400 | .0791142 | .0788893 | .0786651 | .0784417 | .0782191 |
| 9.9 | .0779972 | .0777762 | .0775559 | .0773364 | .0771176 | .0768996 | .0766824 | .0764659 | .0762502 | .0760352 |

*Cv/3R*

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 10.0 | 0.0758210 | 0.0756075 | 0.0753948 | 0.0751828 | 0.0749716 | 0.0747611 | 0.0745513 | 0.0743422 | 0.0741339 | 0.0739263 |
| 10.1 | .0737194 | .0735133 | .0733078 | .0731031 | .0728991 | .0726957 | .0724931 | .0722912 | .0720900 | .0718895 |
| 10.2 | .0716897 | .0714905 | .0712921 | .0710943 | .0708973 | .0707009 | .0705051 | .0703101 | .0701157 | .0699220 |
| 10.3 | .0697290 | .0695366 | .0693449 | .0691539 | .0689635 | .0687738 | .0685847 | .0683962 | .0682084 | .0680213 |
| 10.4 | .0678348 | .0676489 | .0674637 | .0672791 | .0670952 | .0669118 | .0667291 | .0665470 | .0663656 | .0661848 |
| 10.5 | .0660045 | .0658249 | .0656459 | .0654676 | .0652898 | .0651126 | .0649361 | .0647601 | .0645847 | .0644100 |
| 10.6 | .0642358 | .0640622 | .0638892 | .0637168 | .0635450 | .0633738 | .0632031 | .0630330 | .0628635 | .0626946 |
| 10.7 | .0625263 | .0623585 | .0621913 | .0620246 | .0618585 | .0616930 | .0615280 | .0613636 | .0611997 | .0610364 |
| 10.8 | .0608737 | .0607115 | .0605498 | .0603887 | .0602281 | .0600681 | .0599086 | .0597496 | .0595912 | .0594333 |
| 10.9 | .0592759 | .0591190 | .0589627 | .0588069 | .0586516 | .0584969 | .0583426 | .0581889 | .0580357 | .0578830 |
| 11.0 | .0577308 | .0575791 | .0574280 | .0572773 | .0571271 | .0569774 | .0568283 | .0566796 | .0565314 | .0563837 |
| 11.1 | .0562365 | .0560898 | .0559436 | .0557978 | .0556526 | .0555078 | .0553635 | .0552197 | .0550763 | .0549334 |
| 11.2 | .0547910 | .0546491 | .0545076 | .0543666 | .0542261 | .0540860 | .0539464 | .0538073 | .0536686 | .0535304 |
| 11.3 | .0533926 | .0532552 | .0531183 | .0529819 | .0528460 | .0527104 | .0525753 | .0524407 | .0523065 | .0521727 |
| 11.4 | .0520394 | .0519065 | .0517740 | .0516420 | .0515104 | .0513792 | .0512484 | .0511181 | .0509882 | .0508587 |
| 11.5 | .0507297 | .0506011 | .0504728 | .0503450 | .0502177 | .0500907 | .0499641 | .0498380 | .0497122 | .0495869 |
| 11.6 | .0494620 | .0493374 | .0492133 | .0490896 | .0489663 | .0488433 | .0487208 | .0485987 | .0484769 | .0483556 |
| 11.7 | .0482346 | .0481140 | .0479938 | .0478740 | .0477546 | .0476356 | .0475169 | .0473987 | .0472808 | .0471633 |
| 11.8 | .0470461 | .0469294 | .0468130 | .0466969 | .0465813 | .0464660 | .0463511 | .0462366 | .0461224 | .0460085 |
| 11.9 | .0458951 | .0457820 | .0456693 | .0455569 | .0454448 | .0453332 | .0452219 | .0451109 | .0450003 | .0448900 |

$C_V/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 12.0 | 0.0447801 | 0.0446705 | 0.0445613 | 0.0444525 | 0.0443439 | 0.0442357 | 0.0441279 | 0.0440204 | 0.0439132 | 0.0438064 |
| 12.1 | .0436999 | .0435937 | .0434879 | .0433824 | .0432772 | .0431724 | .0430679 | .0429637 | .0428599 | .0427563 |
| 12.2 | .0426531 | .0425502 | .0424477 | .0423454 | .0422435 | .0421419 | .0420406 | .0419397 | .0418390 | .0417386 |
| 12.3 | .0416386 | .0415389 | .0414395 | .0413404 | .0412416 | .0411431 | .0410449 | .0409470 | .0408494 | .0407522 |
| 12.4 | .0406552 | .0405585 | .0404621 | .0403660 | .0402703 | .0401748 | .0400796 | .0399847 | .0398901 | .0397957 |
| 12.5 | .0397017 | .0396080 | .0395145 | .0394213 | .0393285 | .0392359 | .0391435 | .0390515 | .0389598 | .0388683 |
| 12.6 | .0387771 | .0386862 | .0385956 | .0385052 | .0384151 | .0383253 | .0382358 | .0381465 | .0380575 | .0379688 |
| 12.7 | .0378803 | .0377921 | .0377042 | .0376166 | .0375292 | .0374421 | .0373552 | .0372686 | .0371823 | .0370962 |
| 12.8 | .0370104 | .0369249 | .0368396 | .0367545 | .0366697 | .0365852 | .0365009 | .0364169 | .0363331 | .0362496 |
| 12.9 | .0361664 | .0360834 | .0360006 | .0359181 | .0358358 | .0357538 | .0356720 | .0355904 | .0355091 | .0354281 |
| 13.0 | .0353473 | .0352667 | .0351864 | .0351063 | .0350264 | .0349468 | .0348674 | .0347883 | .0347094 | .0346307 |
| 13.1 | .0345523 | .0344741 | .0343961 | .0343184 | .0342409 | .0341636 | .0340865 | .0340097 | .0339331 | .0338567 |
| 13.2 | .0337805 | .0337046 | .0336289 | .0335534 | .0334782 | .0334031 | .0333283 | .0332537 | .0331793 | .0331051 |
| 13.3 | .0330312 | .0329575 | .0328840 | .0328107 | .0327376 | .0326647 | .0325920 | .0325196 | .0324474 | .0323753 |
| 13.4 | .0323035 | .0322319 | .0321605 | .0320893 | .0320183 | .0319475 | .0318770 | .0318066 | .0317364 | .0316665 |
| 13.5 | .0315967 | .0315272 | .0314578 | .0313886 | .0313197 | .0312509 | .0311824 | .0311140 | .0310458 | .0309779 |
| 13.6 | .0309101 | .0308425 | .0307751 | .0307079 | .0306409 | .0305741 | .0305075 | .0304411 | .0303748 | .0303088 |
| 13.7 | .0302429 | .0301773 | .0301118 | .0300465 | .0299814 | .0299164 | .0298517 | .0297872 | .0297228 | .0296586 |
| 13.8 | .0295946 | .0295308 | .0294671 | .0294037 | .0293404 | .0292773 | .0292144 | .0291516 | .0290890 | .0290266 |
| 13.9 | .0289644 | .0289024 | .0288405 | .0287788 | .0287173 | .0286559 | .0285948 | .0285338 | .0284729 | .0284123 |

$Cv/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 14.0 | 0.0283518 | 0.0282915 | 0.0282313 | 0.0281713 | 0.0281115 | 0.0280519 | 0.0279924 | 0.0279331 | 0.0278739 | 0.0278149 |
| 14.1 | .0277561 | .0276975 | .0276390 | .0275806 | .0275225 | .0274645 | .0274066 | .0273489 | .0272914 | .0272341 |
| 14.2 | .0271769 | .0271198 | .0270629 | .0270062 | .0269496 | .0268932 | .0268369 | .0267808 | .0267249 | .0266691 |
| 14.3 | .0266134 | .0265579 | .0265026 | .0264474 | .0263924 | .0263375 | .0262828 | .0262282 | .0261737 | .0261194 |
| 14.4 | .0260653 | .0260113 | .0259575 | .0259038 | .0258502 | .0257968 | .0257436 | .0256905 | .0256375 | .0255847 |
| 14.5 | .0255320 | .0254795 | .0254271 | .0253748 | .0253227 | .0252708 | .0252190 | .0251673 | .0251157 | .0250643 |
| 14.6 | .0250130 | .0249619 | .0249109 | .0248601 | .0248094 | .0247588 | .0247083 | .0246580 | .0246079 | .0245578 |
| 14.7 | .0245079 | .0244582 | .0244085 | .0243590 | .0243097 | .0242604 | .0242113 | .0241624 | .0241135 | .0240648 |
| 14.8 | .0240162 | .0239678 | .0239195 | .0238713 | .0238232 | .0237753 | .0237275 | .0236798 | .0236322 | .0235848 |
| 14.9 | .0235375 | .0234903 | .0234432 | .0233963 | .0233495 | .0233028 | .0232563 | .0232098 | .0231635 | .0231174 |
| 15.0 | .0230713 | .0230253 | .0229795 | .0229338 | .0228882 | .0228428 | .0227974 | .0227522 | .0227071 | .0226621 |
| 15.1 | .0226172 | .0225725 | .0225279 | .0224833 | .0224389 | .0223947 | .0223505 | .0223064 | .0222625 | .0222187 |
| 15.2 | .0221750 | .0221314 | .0220879 | .0220445 | .0220013 | .0219581 | .0219151 | .0218722 | .0218294 | .0217867 |
| 15.3 | .0217441 | .0217016 | .0216592 | .0216170 | .0215748 | .0215328 | .0214909 | .0214490 | .0214073 | .0213657 |
| 15.4 | .0213242 | .0212828 | .0212415 | .0212004 | .0211593 | .0211183 | .0210775 | .0210367 | .0209960 | .0209555 |
| 15.5 | .0209150 | .0208747 | .0208345 | .0207943 | .0207543 | .0207144 | .0206745 | .0206348 | .0205952 | .0205557 |
| 15.6 | .0205162 | .0204769 | .0204377 | .0203985 | .0203595 | .0203206 | .0202818 | .0202430 | .0202044 | .0201659 |
| 15.7 | .0201274 | .0200891 | .0200508 | .0200127 | .0199747 | .0199367 | .0198988 | .0198611 | .0198234 | .0197858 |
| 15.8 | .0197484 | .0197110 | .0196737 | .0196365 | .0195994 | .0195624 | .0195254 | .0194886 | .0194519 | .0194152 |
| 15.9 | .0193787 | .0193422 | .0193059 | .0192696 | .0192334 | .0191973 | .0191613 | .0191254 | .0190896 | .0190538 |

$C_v/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 16.0 | 0.0190182 | 0.0189826 | 0.0189471 | 0.0189118 | 0.0188765 | 0.0188413 | 0.0188061 | 0.0187711 | 0.0187361 | 0.0187013 |
| 16.1 | .0186665 | .0186318 | .0185972 | .0185627 | .0185283 | .0184939 | .0184596 | .0184255 | .0183914 | .0183574 |
| 16.2 | .0183234 | .0182896 | .0182558 | .0182221 | .0181885 | .0181550 | .0181246 | .0180882 | .0180550 | .0180218 |
| 16.3 | .0179887 | .0179556 | .0179227 | .0178898 | .0178570 | .0178243 | .0177917 | .0177592 | .0177267 | .0176943 |
| 16.4 | .0176620 | .0176298 | .0175976 | .0175655 | .0175335 | .0175016 | .0174698 | .0174380 | .0174063 | .0173747 |
| 16.5 | .0173432 | .0173117 | .0172803 | .0172490 | .0172178 | .0171866 | .0171555 | .0171245 | .0170936 | .0170627 |
| 16.6 | .0170319 | .0170012 | .0169706 | .0169400 | .0169095 | .0168791 | .0168488 | .0168185 | .0167883 | .0167582 |
| 16.7 | .0167281 | .0166981 | .0166682 | .0166383 | .0166086 | .0165789 | .0165492 | .0165197 | .0164902 | .0164608 |
| 16.8 | .0164314 | .0164021 | .0163729 | .0163438 | .0163147 | .0162857 | .0162568 | .0162279 | .0161991 | .0161704 |
| 16.9 | .0161417 | .0161131 | .0160846 | .0160561 | .0160277 | .0159994 | .0159711 | .0159429 | .0159148 | .0158867 |
| 17.0 | .0158587 | .0158308 | .0158029 | .0157751 | .0157474 | .0157197 | .0156921 | .0156646 | .0156371 | .0156097 |
| 17.1 | .0155823 | .0155550 | .0155278 | .0155007 | .0154736 | .0154465 | .0154196 | .0153927 | .0153658 | .0153390 |
| 17.2 | .0153123 | .0152857 | .0152591 | .0152325 | .0152060 | .0151796 | .0151533 | .0151270 | .0151008 | .0150746 |
| 17.3 | .0150485 | .0150224 | .0149964 | .0149705 | .0149446 | .0149188 | .0148931 | .0148674 | .0148418 | .0148162 |
| 17.4 | .0147907 | .0147652 | .0147398 | .0147145 | .0146892 | .0146640 | .0146388 | .0146137 | .0145886 | .0145636 |
| 17.5 | .0145387 | .0145138 | .0144890 | .0144642 | .0144395 | .0144148 | .0143902 | .0143657 | .0143412 | .0143168 |
| 17.6 | .0142924 | .0142681 | .0142438 | .0142196 | .0141954 | .0141713 | .0141473 | .0141233 | .0140994 | .0140755 |
| 17.7 | .0140516 | .0140278 | .0140041 | .0139804 | .0139568 | .0139333 | .0139098 | .0138863 | .0138629 | .0138395 |
| 17.8 | .0138162 | .0137930 | .0137698 | .0137467 | .0137236 | .0137005 | .0136775 | .0136546 | .0136317 | .0136089 |
| 17.9 | .0135861 | .0135633 | .0135406 | .0135180 | .0134954 | .0134729 | .0134504 | .0134280 | .0134056 | .0133833 |

$C_v/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 18.0 | 0.0133610 | 0.0133387 | 0.0133165 | 0.0132944 | 0.0132723 | 0.0132503 | 0.0132283 | 0.0132064 | 0.0131845 | 0.0131626 |
| 18.1 | .0131408 | .0131191 | .0130974 | .0130757 | .0130541 | .0130326 | .0130110 | .0129896 | .0129682 | .0129468 |
| 18.2 | .0129255 | .0129042 | .0128830 | .0128618 | .0128407 | .0128196 | .0127985 | .0127775 | .0127566 | .0127357 |
| 18.3 | .0127148 | .0126940 | .0126732 | .0126525 | .0126318 | .0126112 | .0125906 | .0125700 | .0125495 | .0125291 |
| 18.4 | .0125087 | .0124883 | .0124680 | .0124477 | .0124275 | .0124073 | .0123871 | .0123670 | .0123470 | .0123270 |
| 18.5 | .0123070 | .0122871 | .0122672 | .0122473 | .0122275 | .0122078 | .0121881 | .0121684 | .0121487 | .0121291 |
| 18.6 | .0121096 | .0120901 | .0120706 | .0120512 | .0120318 | .0120125 | .0119932 | .0119739 | .0119547 | .0119355 |
| 18.7 | .0119164 | .0118973 | .0118783 | .0118593 | .0118403 | .0118214 | .0118025 | .0117836 | .0117648 | .0117460 |
| 18.8 | .0117273 | .0117086 | .0116900 | .0116714 | .0116528 | .0116342 | .0116157 | .0115973 | .0115789 | .0115605 |
| 18.9 | .0115422 | .0115239 | .0115056 | .0114874 | .0114692 | .0114511 | .0114330 | .0114149 | .0113969 | .0113789 |
| 19.0 | .0113609 | .0113430 | .0113251 | .0113073 | .0112895 | .0112717 | .0112540 | .0112363 | .0112186 | .0112010 |
| 19.1 | .0111834 | .0111659 | .0111484 | .0111309 | .0111135 | .0110961 | .0110787 | .0110614 | .0110441 | .0110268 |
| 19.2 | .0110096 | .0109924 | .0109753 | .0109582 | .0109411 | .0109241 | .0109071 | .0108901 | .0108732 | .0108563 |
| 19.3 | .0108394 | .0108226 | .0108058 | .0107890 | .0107723 | .0107556 | .0107390 | .0107223 | .0107057 | .0106892 |
| 19.4 | .0106727 | .0106562 | .0106397 | .0106233 | .0106069 | .0105906 | .0105743 | .0105580 | .0105417 | .0105255 |
| 19.5 | .0105093 | .0104932 | .0104771 | .0104610 | .0104449 | .0104289 | .0104129 | .0103970 | .0103811 | .0103652 |
| 19.6 | .0103493 | .0103335 | .0103177 | .0103019 | .0102862 | .0102705 | .0102549 | .0102392 | .0102236 | .0102081 |
| 19.7 | .0101925 | .0101770 | .0101616 | .0101461 | .0101307 | .0101153 | .0101000 | .0100847 | .0100694 | .0100541 |
| 19.8 | .0100389 | .0100237 | .0100085 | .00999341 | .00997830 | .00996323 | .00994819 | .00993318 | .00991820 | .00990325 |
| 19.9 | .00988833 | .00987344 | .00985858 | .00984375 | .00982894 | .00981417 | .00979943 | .00978472 | .00977003 | .00975538 |

$C_v/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 20.0 | 0.00974076 | 0.00972616 | 0.00971160 | 0.00969706 | 0.00968255 | 0.00966807 | 0.00965362 | 0.00963920 | 0.00962481 | 0.00961044 |
| 20.1 | .00959611 | .00958180 | .00956752 | .00955327 | .00953905 | .00952485 | .00951069 | .00949655 | .00948244 | .00946836 |
| 20.2 | .00945430 | .00944028 | .00942628 | .00941231 | .00939837 | .00938445 | .00937056 | .00935670 | .00934287 | .00932906 |
| 20.3 | .00931528 | .00930153 | .00928781 | .00927411 | .00926044 | .00924679 | .00923317 | .00921958 | .00920602 | .00919248 |
| 20.4 | .00917897 | .00916549 | .00915203 | .00913860 | .00912519 | .00911181 | .00909846 | .00908513 | .00907183 | .00905856 |
| 20.5 | .00904531 | .00903208 | .00901889 | .00900572 | .00899257 | .00897945 | .00896635 | .00895328 | .00894024 | .00892722 |
| 20.6 | .00891423 | .00890126 | .00888831 | .00887539 | .00886250 | .00884963 | .00883679 | .00882397 | .00881118 | .00879841 |
| 20.7 | .00878566 | .00877294 | .00876025 | .00874758 | .00873493 | .00872231 | .00870971 | .00869714 | .00868459 | .00867206 |
| 20.8 | .00865956 | .00864708 | .00863463 | .00862220 | .00860980 | .00859742 | .00858506 | .00857272 | .00856041 | .00854812 |
| 20.9 | .00853586 | .00852362 | .00851140 | .00849921 | .00848704 | .00847489 | .00846277 | .00845067 | .00843859 | .00842654 |
| 21.0 | .00841451 | .00840250 | .00839051 | .00837855 | .00836661 | .00835469 | .00834279 | .00833092 | .00831907 | .00830724 |
| 21.1 | .00829544 | .00828366 | .00827190 | .00826016 | .00824844 | .00823675 | .00822507 | .00821342 | .00820180 | .00819019 |
| 21.2 | .00817861 | .00816704 | .00815550 | .00814399 | .00813249 | .00812101 | .00810956 | .00809813 | .00808672 | .00807533 |
| 21.3 | .00806396 | .00805261 | .00804129 | .00802998 | .00801870 | .00800744 | .00799620 | .00798498 | .00797378 | .00796260 |
| 21.4 | .00795144 | .00794031 | .00792919 | .00791810 | .00790702 | .00789597 | .00788494 | .00787393 | .00786293 | .00785196 |
| 21.5 | .00784101 | .00783008 | .00781917 | .00780828 | .00779741 | .00778656 | .00777573 | .00776492 | .00775413 | .00774336 |
| 21.6 | .00773262 | .00772189 | .00771118 | .00770049 | .00768982 | .00767917 | .00766853 | .00765792 | .00764733 | .00763676 |
| 21.7 | .00762621 | .00761567 | .00760516 | .00759467 | .00758419 | .00757373 | .00756330 | .00755288 | .00754248 | .00753210 |
| 21.8 | .00752174 | .00751140 | .00750108 | .00749078 | .00748049 | .00747022 | .00745998 | .00744975 | .00743954 | .00742935 |
| 21.9 | .00741918 | .00740902 | .00739889 | .00738877 | .00737867 | .00736859 | .00735853 | .00734849 | .00733846 | .00732846 |

$Cv/3R$

| $x$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|---|
| 22.0 | 0.00731847 | 0.00730850 | 0.00729854 | 0.00728861 | 0.00727869 | 0.00726879 | 0.00725891 | 0.00724905 | 0.00723921 | 0.00722938 |
| 22.1 | .00721957 | .00720978 | .00720001 | .00719025 | .00718051 | .00717079 | .00716109 | .00715140 | .00714173 | .00713208 |
| 22.2 | .00712245 | .00711283 | .00710323 | .00709365 | .00708409 | .00707454 | .00706501 | .00705550 | .00704600 | .00703652 |
| 22.3 | .00702706 | .00701762 | .00700819 | .00699878 | .00698939 | .00698001 | .00697065 | .00696130 | .00695198 | .00694267 |
| 22.4 | .00693337 | .00692409 | .00691483 | .00690559 | .00689636 | .00688715 | .00687795 | .00686878 | .00685961 | .00685047 |
| 22.5 | .00684134 | .00683222 | .00682313 | .00681405 | .00680498 | .00679593 | .00678690 | .00677788 | .00676888 | .00675990 |
| 22.6 | .00675093 | .00674197 | .00673303 | .00672411 | .00671521 | .00670632 | .00669744 | .00668858 | .00667974 | .00667091 |
| 22.7 | .00666210 | .00665330 | .00664452 | .00663576 | .00662701 | .00661827 | .00660955 | .00660085 | .00659216 | .00658348 |
| 22.8 | .00657483 | .00656618 | .00655755 | .00654894 | .00654034 | .00653176 | .00652319 | .00651464 | .00650610 | .00649758 |
| 22.9 | .00648907 | .00648058 | .00647210 | .00646363 | .00645518 | .00644675 | .00643833 | .00642992 | .00642153 | .00641316 |
| 23.0 | .00640480 | .00639645 | .00638812 | .00637980 | .00637150 | .00636321 | .00635493 | .00634667 | .00633843 | .00633020 |
| 23.1 | .00632198 | .00631378 | .00630559 | .00629741 | .00628925 | .00628110 | .00627297 | .00626485 | .00625675 | .00624866 |
| 23.2 | .00624058 | .00623252 | .00622447 | .00621643 | .00620841 | .00620041 | .00619241 | .00618443 | .00617647 | .00616852 |
| 23.3 | .00616058 | .00615265 | .00614474 | .00613684 | .00612896 | .00612109 | .00611323 | .00610538 | .00609755 | .00608973 |
| 23.4 | .00608193 | .00607414 | .00606636 | .00605860 | .00605085 | .00604311 | .00603539 | .00602768 | .00601998 | .00601229 |
| 23.5 | .00600462 | .00599696 | .00598931 | .00598168 | .00597406 | .00596645 | .00595886 | .00595128 | .00594371 | .00593616 |
| 23.6 | .00592861 | .00592108 | .00591357 | .00590606 | .00589857 | .00589109 | .00588362 | .00587617 | .00586873 | .00586130 |
| 23.7 | .00585388 | .00584648 | .00583909 | .00583171 | .00582434 | .00581699 | .00580965 | .00580232 | .00579500 | .00578770 |
| 23.8 | .00578041 | .00577313 | .00576586 | .00575860 | .00575136 | .00574413 | .00573691 | .00572970 | .00572251 | .00571532 |
| 23.9 | .00570815 | .00570099 | .00569385 | .00568671 | .00567959 | .00567248 | .00566538 | .00565829 | .00565121 | .00564415 |
| 24.0 | .00563710 | | | | | | | | | |

$$\frac{Cv}{3R}=\frac{77.92727}{x^3}\text{ when }x>24$$

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# PUBLICATIONS

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# THE RELATIVE INTENSITIES OF REFLECTION OF X-RAYS FROM THE PRINCIPAL ATOMIC PLANES OF POWDERED SODIUM CLORIDE

by

L. Harris, S. J. Bates and D. A. MacInnes

# THE RELATIVE INTENSITIES OF REFLECTION OF X-RAYS FROM THE PRINCIPAL ATOMIC PLANES OF POWDERED SODIUM CHLORIDE*

By Louis Harris, S. J. Bates, and D. A. MacInnes

## Abstract

Measurements have been made on the relative intensities of reflection of the alpha doublet of characteristic molybdenum x-rays, from powdered sodium chloride, using the modified Bragg apparatus described in a previous communication. Determinations were made with (a) filtered rays and (b) rays reflected from a calcite crystal. In a separate investigation the lines were obtained on photographic plates and their intensities were found photometrically. All three series gave results that are in agreement with the measurements of Bragg, James and Bosanquet on large crystals, after their results are corrected for their determinations of the "extinction" in those crystals. Our experiments thus indicate that results on measurements with 325 mesh powder are as free from the effects of "extinction" as are the results of the workers just mentioned.

REFLECTIONS, or more properly diffractions, from crystals are complicated by the phenomenon of "extinction," i.e., an additional absorption at angles at which reflection takes place. It has been pointed out a number of times that the least ambiguous results in measurements of intensities of reflection should be obtained from powders rather than from single large crystals. Darwin[1] has given a detailed discussion of the phenomenon of extinction, analyzing it into two effects, which will be discussed further below.

The work to be described was undertaken with the purpose of developing a technique for obtaining accurate measurements on intensities of reflection from crystal powders. Three series of determinations of the relative intensities of reflection from the principal atomic planes of sodium chloride were made using three different methods. The results have been corrected to indicate the "reflecting power" of the crystal at the observed points, and compared with the corresponding values of

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* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 184, and from the Gates Chemical Laboratory, California Institute of Technology, No. 102.

[1] Darwin, Phil. Mag. **43**, 800 (1922).

Bragg, James and Bosanquet[2] obtained from corrected measurements from single crystals of rock salt.

Two experimental arrangements were tested. The first of these is given diagrammatically in Fig. 1. X-rays from the water cooled Coolidge tube, which was furnished with a molybdenum target, passed through the slit $S_1$, and the Zirconium filter (Zr), and then to the slit $S_2$, the upper and lower halves of which could be adjusted as to width separately, the rays from the upper half going to the reference crystal and to the ionization chamber $E'$ to which a Bumstead electroscope was attached. The rays which passed through the lower half of slit $S_2$ were further imited by slit $S_3$ and passed on to the pellet of powdered sodium chloride $C$ from which the "reflected" rays were caught in the ionization chamber $E$ and measured by a second Bumstead electroscope. The use of the reference crystal in intensity measurements has been described elsewhere.[3] The pellet of powdered salt, $C$, was continuously oscillated through a small angle by means of an electric motor and a cam designed to yield a uniform angular motion. This produced a greater "randomness" in the orientation of the particles.

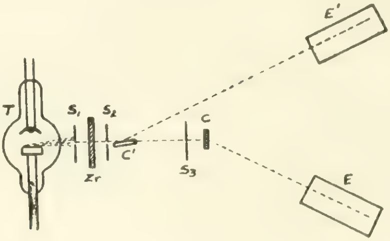

Fig. 1.

A convenient form of flat pellet of the powder (ground to pass through a 325 mesh sieve) was obtained by compressing, in a vice, the sifted material between two closely fitting plungers in a steel cylinder.

With the apparatus as described a series of measurements was made by one of the authors (S. J. B.) on pellets of varying thicknesses of sodium chloride. The averages of several runs are given in column 2 of Table I. The intensity did not vary appreciably with thickness if it was near the optimum value given by the relation $t$ (optimum) $= 1/\mu \sec \theta$, where $t$ is the thickness of the pellet, $\mu$ the linear absorption coefficient of the wave-length in question, and $\theta$ the incident angle of the rays.

[2] Bragg, James and Bosanquet, Phil. Mag. **41**, 308 (1921); **42**, 1 (1921).

[3] MacInnes and Shedlovsky, Phys. Rev., **27**, 130 (1926).

[4] Glockler and Traub, Phys. Zeits., **22**, 345 (1921).

A second series of measurements was later made by the same investigator using filtered x-rays and substituting a photographic plate for the ionization chambers. The intensities were then calculated from accurate photometric determinations made through the kindness of the Mt. Wilson Observatory, using the relations given by Glockler and Traub.[4] On account of the difficulties of the photographic method, the results were not as reproducible nor as trustworthy as those obtained by other methods. The values are, however, given in column 4 of Table I.

On account of the difficulty experienced with the experimental arrangements just described in correcting for general radiation, which was but partly removed by the zirconium screen, a radically different experimental procedure was adopted. A diagram of the modified apparatus is shown in Fig. 2. X-rays from the molybdenum target of the tube $T$, after passing through the slit $S_1$, were reflected from an exceptionally good calcite crystal $C_1$, which was oriented so as to reflect the alpha doublet of the rays through the slit $S_2$, from which the resulting substantially monochromatic rays passed to the powdered crystals $C_3$. The reference crystal $C_2$ was used as in the experiments already described. It was of interest to see to what extent we were successful in obtaining monochromatic x-rays by this apparatus. For that purpose a rock salt crystal was substituted for the powder and the rays passing through slit $S_2$ were analyzed. The results were as follows in arbitrary units of intensity: $\alpha$ doublet 100.0, $\beta$ line 0.00, half wave-length, 2.4, one third wave-length, 1.0. The general radiation was smaller than the experimental error in reading the electroscopes. A third series of intensity measurements with the modified method was made on sodium chloride powder and are given in column 3 of Table I.

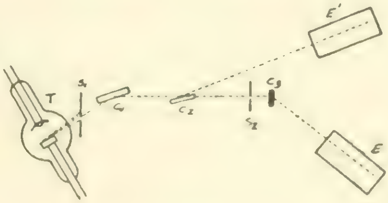

Fig. 2.

The radiation reflected from each plane appears on a photographic plate as a halo, since the numerous particles correctly situated for reflection send out the reflected rays in the form of a hollow cone. If the slit limiting the incident beam were a point, the halo would be a circle. In the case of a rectangular slit, such as was used, the halo is plano convex near the center and becomes circular at greater angles. The exact shapes of the haloes depend on the size of the slit, the thickness of the powder, the distance from the powder to the plate, and the reflecting angle. The radius of a halo is given by the expression $l \sin 2\theta$, where $l$ is the length of the arm of the ionization chamber and $2\theta$ the chamber angle, or twice the reflecting angle of the rays. The energy measured in the ionization chamber is the fraction of the halo defined by the height of the chamber slit $a$, that is: $a/2\pi l \sin 2\theta$. In addition, the number of contributing planes from each crystal face must be taken into account. Thus, since $a/2\pi l$ is a constant of the apparatus, the measured values should, therefore, be multiplied by ($\sin 2\theta$/number of reflecting planes).

Furthermore, our results with molybdenum rays and the powder and those of Bragg, James and Bosanquet with rhodium rays and single crystals can be more readily compared if both are converted into the corresponding reflecting powers which depend on the crystal lattice alone. This involves multiplying by two terms which occur in the Darwin[5]-Compton[6] equation: first, a polarization correction $(1+\cos^2 2\theta)$; and second, another function of the angle of reflection, which is $\sin 2\theta$ for a single crystal and $\sin \theta$ for a powder.

TABLE I

*Relative intensities of reflection of x-rays from sodium chloride.* [100] = 100

| Reflecting plane | Filtered source S.J.B. | Reflected source L.H. | Photographic measurements S.J.B. | Bragg, James & Bosanquet. |
|---|---|---|---|---|
| [100] | 100. | 100. | 100. | 100. |
| [111] | 6.1 | 4.5 | 6.8 | 5.3 |
| [110] | 61. | 59. | 73. | 59.5 |
| [222] | 39.5 | 37.5 | 51. | 46. |
| [200] | 28. | 29. | 24. | 31. |
| [311] | 1.4 | 1.5 | —— | 1.4 |

Table I gives a summary of the relative, completely corrected, reflecting powers obtained by the different methods outlined in this article, and also the corresponding values given by Bragg, James and Bosanquet, whose nomenclature for indicating the reflecting plane and order has been followed. The first order reflection from the cube face [100] has been arbitrarily given the value 100.

## DISCUSSION OF RESULTS

The photographic measurements agree with the others in order of magnitude. They are, however, the least trustworthy because of the aforementioned difficulties with the photographic method.

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[5] C. G. Darwin, Phil. Mag. **27**, 675 (1914).

[6] A. H. Compton, Phys. Rev. **9**, 29 (1917).

The other measurements of the relative intensities are in good agreement among themselves and with the values of Bragg, James and Bosanquet, who have used an entirely different method for obtaining their results and also a different wave-length of x-rays.

This latter agreement indicates that our reflections from powders of 325 mesh were as free from "extinction" effects as those obtained from single crystals of rock salt by the method of Bragg, James and Bosanquet.[2] They roughened the surface of their crystals by grinding, reducing what Darwin[1] terms "primary extinction" as much as possible, and corrected for "secondary extinction"[*] with the aid of measurements made with thin crystal slips of varying thicknesses.

CAMBRIDGE, MASSACHUSETTS AND PASADENA, CALIFORNIA,
May 4, 1926.

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[*] "Primary extinction" occurs in homogeneous (perfect) crystals and is due to the diminishing of the energy in the incident beam by interference with doubly reflected rays, which are parallel to, but of exactly opposite phase to the incident beam. " 'Secondary extinction' may be calculated by allowing for the ordinary absorption of the incident beam and in addition subtracting from it the amount of reflection . . . .from homogeneous blocks oriented at the proper angle in the conglomerate crystal." (Darwin, ibid., p. 817).

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# THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. V. A CONSTANT CURRENT APPARATUS

by

Duncan A. MacInnes, Irving A. Cowperthwaite and
Kenneth C. Blanchard

[Reprint from the Journal of the American Chemical Society, **48**, 1909 (1926).]

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 185]

# THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS.[1] V. A CONSTANT CURRENT APPARATUS

BY DUNCAN A. MACINNES, IRVING A. COWPERTHWAITE AND KENNETH C. BLANCHARD

RECEIVED MAY 10, 1926     PUBLISHED JULY 6, 1926

In the determination of a transference number $T$ from the motion of a single boundary the results are computed from the formula

$$T = VF/\phi it$$

$V$ being the volume through which the boundary has swept, $\phi$ the volume containing a gram equivalent, $F$ is the faraday, and $i$ and $t$ are, respectively, the current and time. It has not, in this work, been found convenient to obtain the product $it$ with a coulometer, since the number of coulombs is too small to measure with accuracy. It has, therefore, been necessary, until our most recent work, to keep the current $i$ constant by hand regulation. Since the solution whose transference numbers are to be measured is gradually replaced by indicator solutions which have lower conductances, the applied potential must be gradually increased if the current is to remain constant. This increase is accomplished by shifting the sliding contact of a rheostat shunting a portion of the storage cells used to supply the voltage. Hand regulation was found to be very tedious, and, especially, as readings of the position of the boundary must be made from time to time, not always accurate. We therefore decided to devise an apparatus for the automatic adjustment of the current. This apparatus has proved to be so satisfactory in operation that it should undoubtedly be useful in other connections.

The device finally adopted is shown in Fig. 1. Current is furnished to transference numbers, it is evident that the movement of the boundary past a graduation mark must have been read, at least in the case of the positive ion, to the nearest second and, also, that the current must have been constant in this interval, within the range of error of the measurements, which was about 0.02%. The sum of the average values of the two transference numbers is 0.5122 + 0.4872 = 0.9994, or within 0.06% of unity. The only previously recorded value for a transference number of potassium nitrate (0.501 for the positive ion) is given by Denison and Steele;[5] this is evidently in error. A series of measurements on transference numbers of a series of nitrates, which present peculiarities which are interesting in the light of the modern theories of electrolytic dissociation, is now in progress.

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[1] The papers that have already appeared in this series are: I. MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923); II. Smith and MacInnes, *ibid.*, **46**, 1398 (1924); III. MacInnes and Brighton, *ibid.*, **47**, 994 (1925); IV. Smith and MacInnes, *ibid.*, **47**, 1009 (1925).

The authors are indebted to the Warren Fund of the American Academy of Arts and Sciences for an appropriation which was of great assistance in this work.

## Summary

An apparatus involving a photo-electric relay system is described. This device maintains a constant current, within 0.02–0.03%, through a moving-boundary apparatus, the resistance of which steadily increases during a determination. Data are given on the moving-boundary measurements on potassium nitrate solutions which indicate that regulation to that precision has been attained in practice.

CAMBRIDGE, MASSACHUSETTS

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[5] Denison and Steele, *Trans. Roy. Soc. London.*, **205A**, 449 (1906).

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# PUBLICATIONS

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# A METHOD FOR DIFFERENTIAL POTENTIOMETRIC TITRATION

by

D. A. MacInnes and P. T. Jones

[Reprint from the Journal of the American Chemical Society, **48**, 2831 (1926).]

[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 186]

# A METHOD FOR DIFFERENTIAL POTENTIOMETRIC TITRATION

### By D. A. MacInnes and Paul T. Jones

Received August 30, 1926 Published November 5, 1926

It has been repeatedly shown[1] that the data obtained from potentiometric titrations can be more readily interpreted if, instead of plotting the electromotive force, $E$, against the volume of reagent, $V$, as is the usual practice, the tangent to that curve, $\Delta E/\Delta V$, is plotted against $V$. The end of the titration appears in the first type of curve as a point of inflection which is not always clearly defined. In the second type of curve, the end of the titration is an unmistakable, sharp maximum. D. C. Cox,[2] in a recent paper, has described an ingenious method for obtaining, by direct experiment, data which are related closely to $\Delta E/\Delta V$. Briefly, his method consists in titration from two burets into two beakers, each of which contains an electrode and half of the solution to be titrated. The beakers are connected electrically by means of a piece of wet filter paper. During the titration one of the burets is kept a small difference of titer, say 0.2 cc., behind the other. The potential readings are therefore those of concentration cells with liquid junctions. His method is restricted for practical use by the necessity of working with two burets in an unusual manner, and of dividing the solution into two equal portions. Furthermore, the accuracy of the method is greatly affected by slight inaccuracies in readings of, and calibrations of the two burets.

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[1] See especially Hostetter and Roberts, This Journal, **41**, 1341 (1919).

[2] Cox, *ibid.*, **47**, 2138 (1925).

It has occurred to the authors that all the advantages of the method devised by Cox can be retained, and only one buret and beaker used, if a small amount of the solution surrounding one of the electrodes is temporarily kept from mixing with the rest of the solution until after each small increment of the titrating reagent is added. The device shown in Fig. 1 was constructed for that purpose after a number of less satisfactory forms had been tried. It consists of a central tube A carrying an electrode of platinum gauze B, which makes contact with mercury on the inside of the tube. The cap C is connected with the guide tube D by means of solid glass rods. C and D slide loosely on the inner tube A, a projection on which is ground to fit the lower edge of the cap C. When this apparatus is placed in a solution and the cap lowered, the solution around the electrode B is held in place and is not disturbed by vigorous stirring. During a titration the cap is lowered before each addition of reagent and the potential, between Electrode B and Electrode B′ placed in the body of the solution, is determined on a potentiometer.[3] The arrangement is shown diagrammatically in Fig. 2.

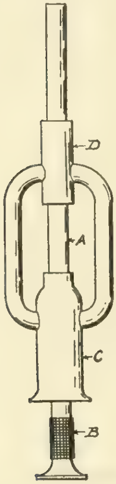

Fig. 1.

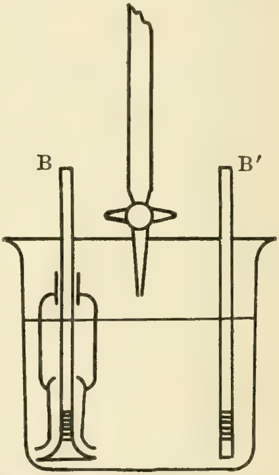

Fig. 2.

A curve for the titration of a strong acid with a strong base, which is quite typical of the results obtained in our experiments, is shown in Fig. 3. In this case hydrochloric acid containing a small quantity of quinhydrone was titrated with sodium hydroxide solution. The addition of the quinhydrone was found to be desirable since it gives a strong oxidation-reduction potential, which has been shown by Biilmann[4] to vary reversibly with the hydrogen-ion activity. The points on the curve were obtained by adding 0.1 cc. to the external solution after the cap C had been lowered, and reading the resulting potential.

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[3] The error due to holding a small portion of the solution temporarily from reacting can readily be shown to be very small. If the cap C is held 1 cc. from 100 cc. of solution the error would be 1% if the 1 cc. were not immediately mixed with the bulk of the solution. However. if the cap is finally lowered when the titration is 99% complete the error is 1% of this or 0.01%. The argument is the same as in the use of "outside" indicators except that in our case the error is not cumulative.

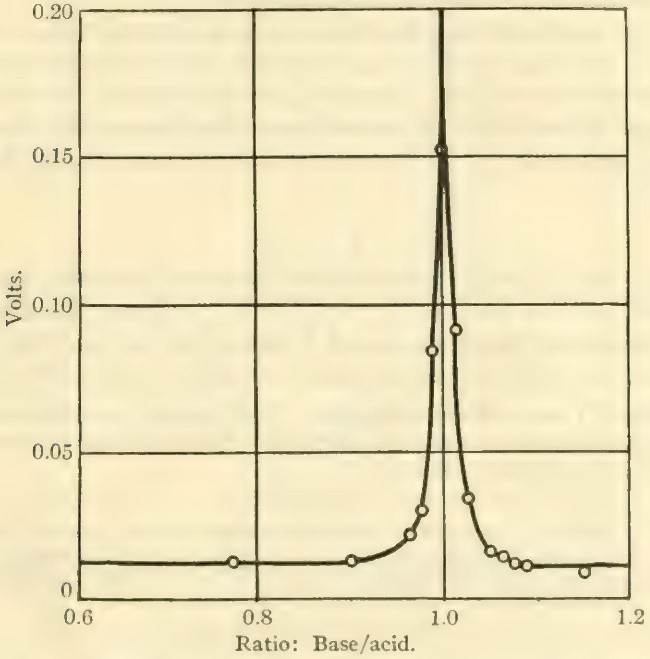

Fig. 3.

Neglecting for the moment the liquid-junction potentials which will be considered below, the theoretical form of the curve shown in Fig. 3 can be readily derived. Since a small amount of the sodium hydroxide solution is added to the much greater bulk of dilute acid, and the acid is steadily converted into salt, the total ion concentration does not change appreciably during the titration. Under these conditions the activity of the acid is proportional to its concentration, at least in reasonably dilute solution.[5] The potential $E$ at one of the electrodes will therefore be $E = E_0 - (RT/F) \log xC$, in which $E_0$ is a constant for the conditions obtaining in the solution, $C$ is the original concentration of the acid and $x$ is the proportion not yet neutralized. The potential between two electrodes with a difference of the proportion of acid $dx$ will thus be $dE = (RT/F) \times (dx/x)$ or for a small finite difference $\Delta x$ the value of $\Delta E/\Delta x$ will be $(RT/F) \times (1/x)$. The descending portion of the curve, which is practically symmetrical with the ascending part can also, with but little error, be computed from the same formula, $x$, however, in this case being the excess of concentration of alkali. The smooth curve which passes through the experimental points has been obtained from the theory as given, allowance being made for initial difference of potential of the electrodes.

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[4] Biilmann, *Trans. Faraday Soc.*, **19**, 676 (1923).

[5] Chow, THIS JOURNAL, **42**, 497 (1920). Harned, *ibid.*, **42**, 1808 (1920).

So far, we have neglected the liquid-junction potential between the two solutions. The type of liquid junction that occurs in these experiments is that of two solutions of the same total ion concentration but with various proportions of two different electrolytes. The formula for these liquid junctions, applicable to two electrolytes with the same degree of dissociation, is

$$E_l = \frac{RT}{F} \ln \frac{x + c}{x' + c} \tag{1}$$

in which $x$ and $x'$ are the proportions of acid not neutralized on the two sides of the junction and $c = (1-N)/(N-N')$, $N'$ being the cation transference number of the pure acid and $N$ that of the salt resulting from the neutralization.[6] For the small differences of $x$ and $x'$ involved, the potentials

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[6] Equation 1 can be derived as follows. To be concrete we will assume that we are dealing with solutions of potassium chloride and hydrochloric acid mixed in various proportions. The differential equation is

$$F\,\mathrm{d}\,E_l = RT(T_{\mathrm{K}}\,\mathrm{d}\ln A_{\mathrm{K}} + T_{\mathrm{H}}\,\mathrm{d}\ln A_{\mathrm{H}} - T_{\mathrm{Cl}}\,\mathrm{d}\ln A_{\mathrm{Cl}}) \tag{2}$$

in which $T_{\mathrm{K}}$, $T_{\mathrm{H}}$ and $T_{\mathrm{Cl}}$ are the transference numbers and $A_{\mathrm{K}}$, $A_{\mathrm{H}}$ and $A_{\mathrm{Cl}}$ are the activities, *in the mixture of solutions*, of the ions represented by the subscripts. Since $A_{\mathrm{Cl}}$ is constant throughout the solution $\mathrm{d}\ln A_{\mathrm{Cl}} = 0$. In such a mixture

$$T_{\mathrm{K}} = \frac{N(1 - N')}{(N - N') + (1 - N)/x}$$

[see MacInnes, THIS JOURNAL, **47**, 1922 (1925)] in which $N$ and $N'$ are, respectively, the cation transference numbers in pure potassium chloride and hydrochloric acid solutions, and $x$ is the proportion of potassium chloride in the electrolyte mixture. The corresponding value for $T_N$ is

$$T_N = \frac{N'(1 - N)}{(N' - N) + (1 - N')/(1 - x)}.$$

Since in these solutions the activities of the cations are proportional to the values of $x$ and $(1 - x)$, Equation 2 may now be written

$$F\,\mathrm{d}\,E_l = RT\left[\frac{N(1 - N')}{(N - N') + (1 - N)/x}\,\mathrm{d}\ln x + \frac{N'(1 - N)}{(N' - N) + (1 - N')/(1 - x)}\,\mathrm{d}\ln(1 - x)\right]$$

which may be simplified to

$$\mathrm{d}\,E_l = \frac{RT}{F}\,\frac{dx}{x + \dfrac{1 - N}{N - N'}}$$

are negligible for our present purpose, since for the titration of hydrochloric acid with sodium hydroxide they vary from 0.3 to 0.9 millivolt on the acid side of the neutralization point, and are 0.3 mv. and less on the alkaline side.

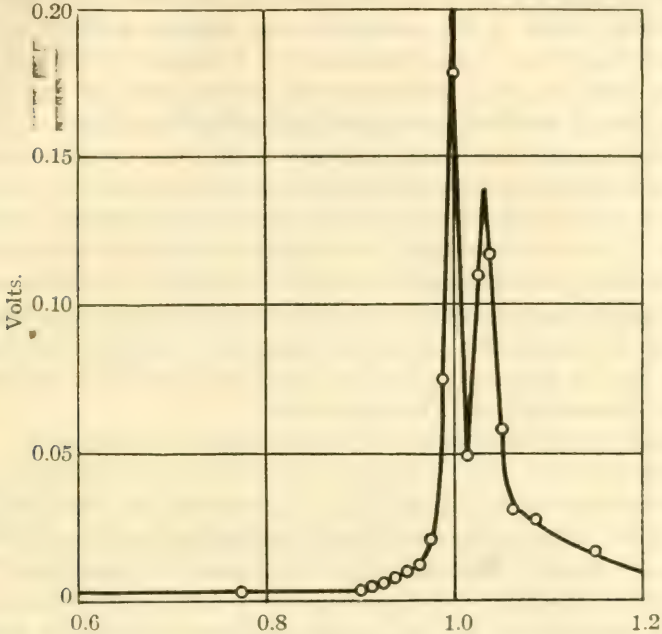

Fig. 4.

With larger quantities of quinhydrone than that used in the experiment whose results are plotted in Fig. 3, the curves take the form shown in Fig. 4, which is typical of many that we have obtained. After the titration of the hydrochloric acid, yielding a sharp maximum identical with that in Fig. 3, another lower but equally sharp maximum is obtained due evidently to a reaction of the base with the hydroquinone. A very similar curve is also obtained when phenolphthalein is substituted for quinhydrone. It is interesting to note that the color change of this indicator occurs after the *second* maximum, showing graphically the need for a correction for the base

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Footnote 6, cont.: If now this is integrated between 0 and 1 we obtain

$$E_t = \frac{RT}{F}\, ln\, \frac{1 - N}{1 - N'}$$

which is a form of the Lewis and Sargent equation. Integrated between the limits $x$ and $x'$ we have

$$E_t = \frac{RT}{F}\, ln\, \frac{x + \dfrac{1 - N}{N - N'}}{x' + \dfrac{1 - N}{N - N'}}$$

reacting with the indicator during such a titration. Phenolphthalein has the further similarity to quinhydrone in yielding an oxidation-reduction potential at the electrodes.

In all the experiments so far described the electrodes were unplatinized, since erratic values of the potentials were obtained unless the platinized electrodes were used in an atmosphere of hydrogen which was carefully kept free from oxygen, a procedure not easy to carry out in ordinary titrations, though worth while in cases having theoretical interest. Vigorous mechanical stirring was found necessary in all these experiments.

The method is especially applicable to oxidation-reduction reactions and is, indeed, serviceable in any case in which potentiometric methods are possible. The curves we have obtained for titrations of ferrous salts with permanganate and dichromate are nearly identical with those of Fig. 3. The end-points can apparently be established more accurately than can be judged by the usual color changes which appear, usually, one drop after the greatest rise of potential. Another paper will deal with this method as adapted to measurements of high precision.

For many practical titrations a potentiometer is unnecessary. The two electrodes shown in Fig. 2 can be connected directly to a galvanometer which remains undeflected, or nearly so, until near the end of the titration, when a slight swing announces the approaching end-point, and a larger one its arrival. In such titrations regular increments of reagent and lifting of the electrode cap after every addition were not found necessary. It is, however, necessary to lift the cap several times during the titration in order that the enclosed solution will have an opportunity to react. In the case of some oxidation-reduction reactions, resistances up to 20,000 ohms were needed in series with even low-sensitivity galvanometers.

## Summary

A method for potentiometric titrations is described, in which only one type of electrode is used, concentration cells being formed during the titration by temporarily isolating a portion of the solution around one of the electrodes. The measured potentials reach a sharp maximum at the end of the titration. The method is capable of high accuracy and is applicable in every case in which potentiometric technique is possible.

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